

*Organometallic and Organometalloidal Fluorine Compounds. Part XII.**
Bistrifluoromethylphosphinic Acid and Related Phosphorus Oxy-
acids.

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Bistrifluoromethylphosphinic acid, $(\text{CF}_3)_2\text{PO}\cdot\text{OH}$, is conveniently prepared by hydrolysis of $(\text{CF}_3)_3\text{PCl}_2$ or $(\text{CF}_3)_2\text{PCl}_3$. It is the strongest acid of phosphorus ($K > 10^{-1}$), and conductivity measurements in acetic acid solution show it to be one of the strongest known acids: the order of decreasing strength, with approximate relative strengths shown in parentheses, is HClO_4 (360) $>$ $(\text{CF}_3)_2\text{PO}\cdot\text{OH}$ (250) $>$ HBr (180) $>$ H_2SO_4 (32) $>$ $\text{CF}_3\cdot\text{PO}(\text{OH})_2$, HCl (9) $>$ $(\text{CF}_3)_2\text{AsO}\cdot\text{OH}$ (3.5) $>$ $\text{CF}_3\cdot\text{AsO}(\text{OH})_2$ (2.5) $>$ $\text{CF}_3\cdot\text{CO}_2\text{H}$, HNO_3 , $\text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$ (1).

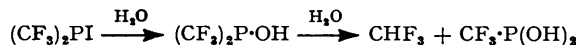
Trifluoromethylphosphonous acid disproportionates in concentrated aqueous solution to yield trifluoromethylphosphine and trifluoromethylphosphonic acid, and the anhydrous acid cannot be isolated. The phosphonous acid has weak reducing properties and is moderately strong ($K = 9.8 \times 10^{-2}$). Infrared spectroscopic studies of the P:O bond in trifluoromethylphosphorus compounds are included.

OXIDATIVE hydrolysis of the compounds $\text{CF}_3\cdot\text{PX}_2$ or $(\text{CF}_3)_2\text{PX}$ ($\text{X} = \text{Cl}$ or I), or controlled hydrolysis of tristrifluoromethylphosphine followed by oxidation, yields the white crystalline trifluoromethylphosphonic acid, $\text{CF}_3\cdot\text{PO}(\text{OH})_2$, which is strong and dibasic (Part X, Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3598). A second acid, trifluoromethylphosphonous acid, $\text{CF}_3\cdot\text{P}(\text{OH})_2$, is also obtained in solution by the aqueous hydrolysis of compounds of the type $\text{CF}_3\cdot\text{PX}_2$ or $(\text{CF}_3)_2\text{PX}$; this acid is volatile with water vapour at low pressures, is monobasic, and yields a sodium salt whose infrared spectrum shows its structure to be $\text{CF}_3\cdot\text{PH}(\text{:O})(\text{ONa})$ rather than $\text{CF}_3\cdot\text{P}(\text{OH})(\text{ONa})$. The present communication describes the preparation and characterisation of a further acid, bistrifluoromethylphosphinic acid, $(\text{CF}_3)_2\text{PO}\cdot\text{OH}$, and also experiments which serve to characterise more fully

* Part XI, Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3896.

trifluoromethyl-phosphonous and -phosphonic acids, and to establish their inter-relationship.

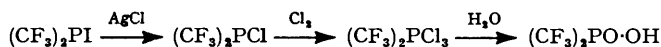
By analogy with trifluoromethyl-phosphonous and -phosphonic acids, one route to bistrifluoromethylphosphinic acid would be by oxidation of bistrifluoromethylphosphinous acid, but earlier studies (Parts X, XI, *loc. cit.*) have shown that the last acid is unstable in aqueous solution and decomposes to yield fluoroform and trifluoromethylphosphonous acid, *e.g.*,



This is in marked contrast to the hydrolysis of dialkylmonohalogenophosphines which yields the dialkylphosphinic acid and the dialkylphosphine (Dorken, *Ber.*, 1888, **21**, 1505; Michaelis and Gleichmann, *Ber.*, 1882, **15**, 801):



A dialkylphosphinous acid has not yet been reported. An alternative route to bistrifluoromethylphosphinic acid was sought and found in the hydrolysis of bistrifluoromethylphosphorus trichloride:

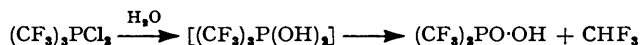


The reaction of chlorine with chlorobistrifluoromethylphosphine is exothermic and is best effected in the liquid phase at low temperature. The trichloride (b. p. *ca.* 107°) is less volatile than tristrifluoromethylphosphorus dichloride (b. p. 80°; Part VII, Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565). Evaporation of its hydrolysate to dryness leaves no residue, thus showing that bistrifluoromethylphosphinic acid is volatile in water vapour like trifluoromethylphosphonous acid. The acid was isolated by formation of its water-soluble silver salt, which could be recrystallised from organic solvents. When heated under reduced pressure with concentrated sulphuric acid, the silver salt yielded a distillate of the viscous, colourless, bistrifluoromethylphosphinic acid. The acid is stable to distillation at atmospheric pressure (b. p. 182°/760 mm.), fumes in air, and is a strong monobasic acid. By contrast, dimethylphosphinic acid (m. p. 87°) is a very weak acid (Kabachnik and Shepeleva, *Izvest. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk*, 1949, **1**, 56; *Chem. Abs.*, 1949, **43**, 5739; Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3381). Only one mole of fluoroform per mole of acid is liberated by reaction of bistrifluoromethylphosphinic acid with an excess of aqueous sodium hydroxide, since the alkali-stable trifluoromethylphosphonic acid is produced:



Loss of fluoroform begins at pH > 8.7.

A more convenient synthesis of bistrifluoromethylphosphinic acid utilises the readily-accessible tristrifluoromethylphosphine, which reacts smoothly with chlorine to give tristrifluoromethylphosphorus dichloride (Part VII, *loc. cit.*). Aqueous hydrolysis of the last compound occurs quantitatively according to the equation



The expected instability of the intermediate $(\text{CF}_3)_3\text{P}(\text{OH})_2$ is confirmed by the fact that tristrifluoromethylphosphine oxide, prepared by reaction of tristrifluoromethylphosphorus dichloride with anhydrous oxalic acid, yields bistrifluoromethylphosphinic acid when treated with water (Paul, following note). The difference between trifluoromethyl compounds and alkyl or aryl compounds is illustrated by the hydrolysis of R_3PX_2 (R = alkyl or aryl, X = halogen or pseudo-halogen), which yields phosphine oxides which are stable in water and form stable hydrates (*e.g.*, Steinkopf, Buckhein, and Krasser, *Ber.*, 1921, **54**, 1024; Michaelis and Soden, *Annalen*, 1885, **229**, 306). Bistrifluoromethylphosphinic acid readily yields a crystalline aniline salt which, since it decomposes when heated, is best characterised

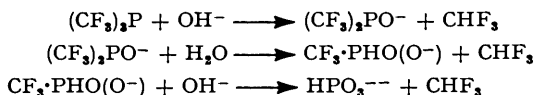
by means of its infrared spectrum (C.S. No. 142).* The salt shows an acid reaction in aqueous solution (pH *ca.* 3), and can be titrated with aqueous sodium hydroxide.

Hydrolysis of tristrifluoromethylphosphorus dichloride with aqueous base yields trifluoromethylphosphonic acid together with two molecular proportions of fluoroform :

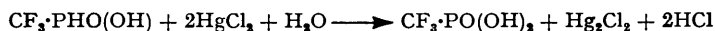


This forms a convenient method for the preparation of trifluoromethylphosphonic acid and is an alternative to the several routes described earlier (Parts X and XI, *loc. cit.*). The preparation of the acid from the iodo-compounds $\text{CF}_3\cdot\text{PI}_2$ and $(\text{CF}_3)_2\text{PI}$ has been used on a larger scale than hitherto, and is somewhat more convenient than the preparation from tristrifluoromethylphosphine, since the iodo-compounds can be manipulated in conventional apparatus. Trifluoromethylphosphonic acid has been further characterised by formation of its mono- and di-potassium salts, and its mono- and di-aniline salts. The aniline salts are particularly useful, since they can be recrystallised from organic solvents, give well-defined infrared spectra (C.S. Nos. 143 and 144), and can be titrated with aqueous base. The P:O stretching vibration in the infrared for anilinium bistrifluoromethylphosphinate (7.85μ) and mono- (7.97μ) and di-anilinium trifluoromethylphosphonate (8.06μ) can be assigned with less certainty than that for the other trifluoromethyl derivatives (see Table 3), since other strong bands appear in the $7.7\text{--}8.2 \mu$ region. The assignment for the trifluoromethylphosphonic acid salts is supported by the fact that the shift in P:O vibration from the mono- to the di-salt is similar to that observed for the mono- and di-sodium and -potassium salts (Table I). The N-H stretching vibration in the infrared spectrum of the aniline salts moves from the usual region near 3.0μ to the amine-salt region at longer wavelength [anilinium bistrifluoromethylphosphinate, $3.76, 4.74$; monoanilinium trifluoromethylphosphonate, $3.80, 4.75$; dianilinium trifluoromethylphosphonate, $3.85, 4.63 \mu$].

A continuation of the study of trifluoromethylphosphonous acid has revealed the general properties of this acid and its relationship to other trifluoromethyl phosphorus oxy-acids. In applying the original preparation of trifluoromethylphosphonous acid (Parts X and XI, *loc. cit.*), on a larger scale, vigorous shaking of tristrifluoromethylphosphine with one equivalent of aqueous base is needed to bring about a rapid reaction and prevent hydrolysis of trifluoromethylphosphonous acid by the base which has not reacted :



Trifluoromethylphosphonous acid has been further characterised as its potassium salt. Aqueous solutions of the free acid are obtained by distillation of the alkali-metal salts with dilute sulphuric acid; since fluoroform is liberated from the acid only at $\text{pH} > 11$, the concentration of aqueous solutions of trifluoromethylphosphonous acid can be determined by titration with carbonate-free aqueous alkali. The reducing properties of the acid were studied: it is not oxidised by iodine solution in presence of sodium hydrogen carbonate (cf. phosphorous acid which is oxidised quantitatively under these conditions); saturated mercuric chloride solution gave no immediate precipitate at room temperature (cf. the immediate precipitate with phosphorous acid), but a slow reaction occurred at 60° according to the equation

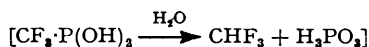


Oxidation of trifluoromethylphosphonous acid by ceric sulphate, potassium iodate, or potassium dichromate solution is slow and is not quite complete after several hours at room temperature; oxidation by acidified potassium permanganate solution at 60° is more rapid and essentially quantitative. These results show that replacement of hydrogen in phosphorous acid by a perfluoroalkyl group considerably lessens the reducing power, but increases the acid strength (see below).

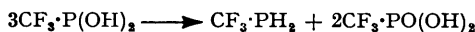
Trifluoromethylphosphonous acid is quantitatively hydrolysed to fluoroform and phos-

* Infrared spectra thus recorded have been deposited with the Society. Photocopies may be obtained, price 3s. 0d. per copy, on application to the General Secretary.

phorous acid when its aqueous solution is heated at 100°. In more concentrated aqueous solution, trifluoromethylphosphonous acid prepared from di-iodotrifluoromethylphosphine similarly yields fluoroform and an equivalent of phosphorous acid when heated at 140°;



an independent side-reaction (8% of the total reaction) produces trifluoromethylphosphine and trifluoromethylphosphonic acid:



This disproportionation of trifluoromethylphosphonous acid also occurs at room temperature, and its relative importance depends mainly upon the concentration of the acid solution. Thus, when di-iodotrifluoromethylphosphine is hydrolysed by the minimum amount of water, to give a very concentrated solution of trifluoromethylphosphonous acid, evaporation of the solution *in vacuo* leaves a white crystalline dibasic acid and trifluoromethylphosphine is produced (Parts VII, XI, *loc. cit.*). The dibasic acid has now been identified as trifluoromethylphosphonic acid by preparation of its mono- and dipotassium salts and mono- and di-aniline salts, and comparison of their infrared spectra with those of authentic samples. The molar ratio of trifluoromethylphosphine to trifluoromethylphosphonic acid is as expected from the last equation. The hydrolysis of di-iodotrifluoromethylphosphine has been studied with varying amounts of water, and when the trifluoromethylphosphonous acid is produced in relatively dilute solution, it is completely volatile in water vapour when evaporated to dryness *in vacuo*, *i.e.*, the disproportionation reaction does not occur. Trifluoromethylphosphonous acid prepared from other sources [*e.g.*, hydrolysis of $(\text{CF}_3)_2\text{PI}$ or $\text{CF}_3 \cdot \text{PCl}_2$] shows similar behaviour.

Disproportionation to trifluoromethylphosphine also occurred during unsuccessful attempts to prepare anhydrous trifluoromethylphosphonous acid by reaction of potassium trifluoromethylphosphonite with phosphoric acid and phosphoric anhydride (cf. preparation of bistrifluoromethylphosphinic acid), and it must be concluded that anhydrous trifluoromethylphosphonous acid cannot be prepared by reactions of this type. This is in accord with the properties of alkyl- and aryl-phosphonous acids; *e.g.*, phenyl-, isoamyl-, and ethyl-phosphonous acids disproportionate according to the equation $3\text{R} \cdot \text{P}(\text{OH})_2 \longrightarrow \text{R} \cdot \text{PH}_2 + 2\text{R} \cdot \text{PO}(\text{OH})_2$ and even phosphorous acid, the parent acid, reacts as $4\text{H}_3\text{PO}_3 \longrightarrow 3\text{H}_3\text{PO}_4 + \text{PH}_3$ when heated (Ananoff, *Ber.*, 1875, 8, 499; Goddard, in Newton Friend's "Textbook of Inorganic Chemistry," Griffin and Co., London, 1936, XI, p. 32; Vigier, *Bull. Soc. chim. France*, 1869, 11, 125).

The tentative assignments for the P:O ($\text{P}^+ \text{--} \text{O}^-$) stretching vibration in the infrared made in Part X for certain trifluoromethylphosphorus compounds are strongly supported by the spectra of the compounds prepared during the present work. The data in Table I show the assignments made for P:O (stretching), C-F (stretching), PO-H (stretching), POH (deformation), and CF_3 (deformation).

A movement of the P:O ($\text{P}^+ \text{--} \text{O}^-$) bond stretching vibration to shorter wave-lengths can be correlated with an increase in its force constant, in its double-bond character, and in the strength of the corresponding oxy-acid. Such a movement is brought about by presence of electronegative groups on the phosphorus atom, as can be seen from Table I, and particularly by comparison of the P:O bands for derivatives of trifluoromethylphosphonic acid (*ca.* 8.0 μ) with the derivatives of the stronger bistrifluoromethylphosphinic acid (*ca.* 7.8 μ). Corresponding shifts to shorter wave-length of the carbonyl frequency in fluoro-carboxylic acids and their derivatives have been noted (*e.g.*, $\text{CH}_3 \cdot \text{CO}_2\text{H}$ 5.85 μ , $\text{CF}_3 \cdot \text{CO}_2\text{H}$ 5.60 μ ; Haszeldine, *Nature*, 1951, 168, 1028). The P:O vibration in the series POF_3 , $(\text{CF}_3)_3\text{PO}$, POCl_3 gives, to a first approximation, a measure of the negativity of the CF_3 group. When three fluorine atoms are attached to the phosphorus, the P:O vibration is at the shortest wave-length (7.07 μ); a CF_3 group is less negative than fluorine, but apparently more electron-attracting than chlorine, since the P:O vibration in the phosphine oxide appears at 7.53 μ . Intermediate values can be expected for compounds such as $\text{CF}_3 \cdot \text{POF}_2$, $(\text{CF}_3)_2\text{POF}$, $\text{CF}_3 \cdot \text{POCl}_2$, and $(\text{CF}_3)_2\text{POCl}$.

Relative Strengths of Trifluoromethyl Oxy-acids.—It has been shown by conductivity

measurements (Part VIII, *loc. cit.*) that trifluoromethylarsonic acid and bistrifluoromethylarsinic acid are almost completely ionised in water, and that in anhydrous acetic acid as solvent the order of acid strength, compared with that of other strong acids, is

TABLE 1. *The P:O stretching vibration.*

	C.S. No.	P:O	Other assignments
$\text{CF}_3\cdot\text{PO}(\text{OK})(\text{OH})$	145	7.93	PO-H 4.3; POH deformation 10.57; CF_3 13.50; C-F 8.32, 8.95
$\text{CF}_3\cdot\text{PO}(\text{OK})_2$	146	8.07	C-F 8.7; CF_3 13.65; no POH bands
$\text{CF}_3\cdot\text{PO}(\text{ONa})(\text{OH})^a$	—	7.99	PO-H 4.25; CF_3 13.5; C-F 8.35
$\text{CF}_3\cdot\text{PO}(\text{ONa})_2^a$	—	8.05	CF_3 13.6; C-F 8.50, 8.75; no POH bands
$\text{CF}_3\cdot\text{PO}(\text{OH})_2$	—	8.0—8.1	C-F 8.69, 8.83; CF_3 13.15
$\text{CF}_3\cdot\text{PH}(\text{O})(\text{ONa})^a$	—	8.05	P-H 4.2; CF_3 13.6; C-F 8.80, 9.00
$(\text{CF}_3)_2\text{PO}\cdot\text{OH}$	147	7.80	PO-H 4.25; CF_3 13.34; C-F 8.3, 8.5, 8.74
$(\text{CF}_3)_2\text{PO}(\text{OAg})$	148	7.84	C-F 8.10, 8.23, 8.67; CF_3 , 13.43; no POH bands
$\text{Ph}\cdot\text{NH}_3^+(\text{CF}_3)_2\text{PO}\cdot\text{O}^-$	142	7.85	C-F 8.65, 8.73
$\text{Ph}\cdot\text{NH}_3^+\text{CF}_3\cdot\text{PO}(\text{OH})\cdot\text{O}^-$	143	7.97	C-F 8.6, 8.95
$(\text{Ph}\cdot\text{NH}_3^+)_2\text{CF}_3\cdot\text{PO}(\text{O}^-)_2$	144	8.06	C-F 9.03
$(\text{CF}_3)_3\text{PO}^b$	—	7.53	C-F 8.27, 8.45; CF_3 13.36
POCl_3^c	—	7.70	
POF_3^d	—	7.07	

^a Parts X and XI, *loc. cit.* ^b Paul, *J.*, 1954, following note. ^c Meyrick and Thompson, *J.*, 1950, 225, report P:O 7.81 μ . ^d Gutowsky and Liehr, *J. Chem. Phys.*, 1952, 20, 1652.

$\text{H}_2\text{SO}_4 > \text{HCl} > (\text{CF}_3)_2\text{AsO}(\text{OH}) > \text{CF}_3\cdot\text{As}(\text{OH})_2 \gg \text{CF}_3\cdot\text{CO}_2\text{H}, \text{HNO}_3, \text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$. These observations have now been extended by measurements on aqueous solutions of trifluoromethylphosphonic, bistrifluoromethylphosphinic, and trifluoromethylphosphonous acids, and by measurements on the first two of these in acetic acid solution.

Bistrifluoromethylphosphinic acid and trifluoromethylphosphonous acid are monobasic, and the graphs of molecular conductivity against square-root of concentration, which are straight lines at low concentrations, lead to values for equivalent conductivity at infinite dilution of 385.7 and 379.0 respectively (see Tables 6 and 7). The graph for trifluoromethylphosphonous acid becomes a curve at higher concentrations (see Table 7). The ionic conductivities of $(\text{CF}_3)_2\text{PO}\cdot\text{O}^-$ and $\text{CF}_3\cdot\text{PHO}(\text{O}^-)$ calculated from the data are 35.9 and 29.1 respectively [cf. $(\text{CF}_3)_2\text{AsO}\cdot\text{O}^-$, 49.6; $\text{CF}_3\cdot\text{AsO}(\text{OH})\cdot\text{O}^-$, 48.1]. The degree of ionisation (α) of bistrifluoromethylphosphinic and trifluoromethylphosphonous acids in aqueous solution as a function of concentration is shown in Table 2.

TABLE 2.*

c	\sqrt{c}	$\text{CF}_3\cdot\text{P}(\text{OH})_2$			$(\text{CF}_3)_2\text{PO}(\text{OH})$		
		λ_c	λ_x	α	λ_c	λ_x	α
0.020	0.1415	349.7	358.5	0.975	365.1	364.7	1.002
0.010	0.1000	354.7	364.5	0.973	371.2	370.9	1.002
0.002	0.0447	366.5	372.5	0.984	379.3	379.0	1.001
0.001	0.0316	370.9	374.4	0.990	381.3	381.0	1.000

* For meaning of c , λ_c , and λ_x see p. 573.

Potentiometric titration gave $K_1 = 6.8 \times 10^{-2}$, $K_2 = 1.2 \times 10^{-4}$ for trifluoromethylphosphonic acid in aqueous solution (Part X, *loc. cit.*). Examination of the conductivity of aqueous solutions of the acid shows that the graph of molecular conductivity against the square-root of concentration is a smooth curve, even at low concentrations. Since λ_c is high (see Table 5) it follows that one hydrogen atom in the phosphonic acid is almost completely ionised, and the extent of ionisation of the second hydrogen atom increases with dilution. This behaviour is consistent with the relatively small ratio of the dissociation constants (*ca.* 575, Part X), and in this respect the acid resembles sulphuric, oxalic, and malonic acids, which also do not give straight lines for $\lambda_c - \sqrt{c}$ plots, and have a small $K_1 : K_2$ ratio. The conductivities of aqueous solutions of mono- and di-potassium trifluoromethylphosphonates have also been studied and the results are shown in Tables 8 and 9. The $\lambda_c - \sqrt{c}$ plot for the monopotassium salt clearly shows the gradual ionisation of the one ionisable hydrogen atom present in the molecule, since a distinct smooth curve is obtained. A similar plot for the dipotassium salt gives a shallow curve which shows an

almost linear relationship at low concentration; the equivalent conductivity at infinite dilution is 256, whence the ionic conductivity for $\frac{1}{2}[\text{CF}_3\cdot\text{PO}_3^{--}]$ is 53.5.

Very approximate values for the ionisation constants of bistrifluoromethylphosphinic and trifluoromethylphosphonous acids, obtained by application of the equation $K =$

FIG. 1.

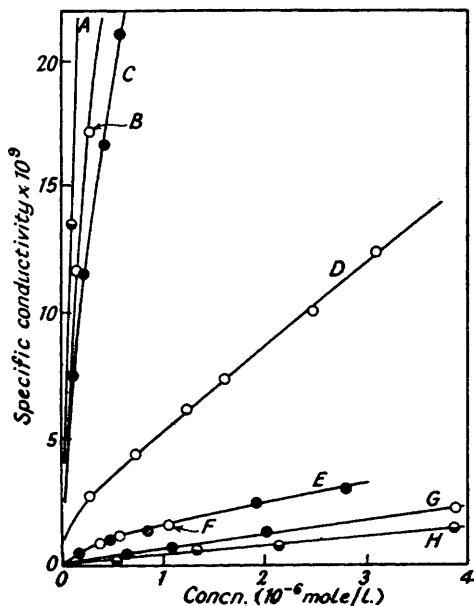


FIG. 2.

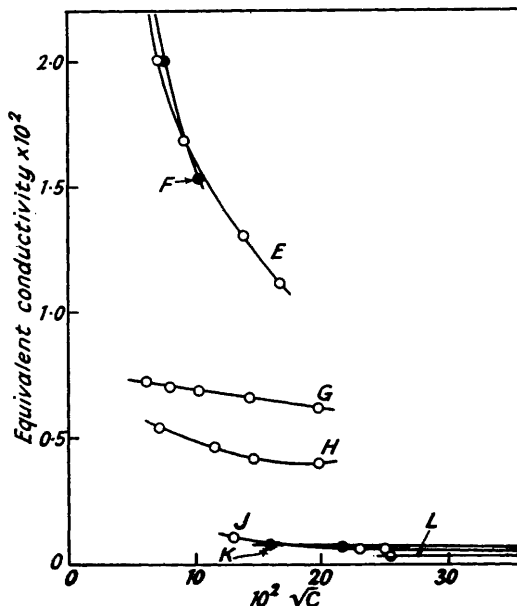
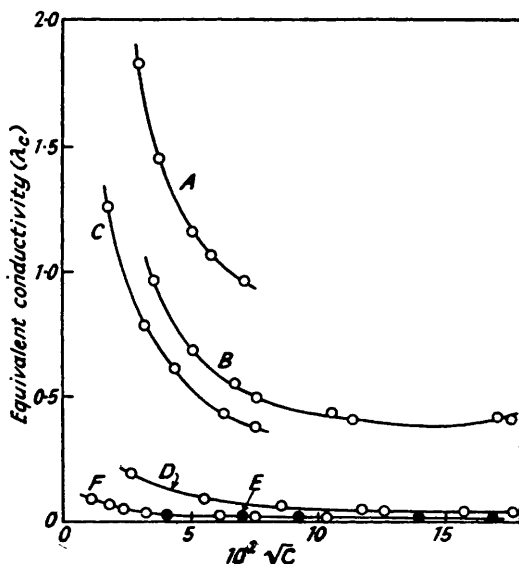


FIG. 3.



Conductivities in acetic acid.

- A, HClO_4 .
- B, $(\text{CF}_3)_2\text{PO}\cdot\text{OH}$.
- C, HBr .
- D, H_2SO_4 .
- E, $\text{CF}_3\cdot\text{PO}(\text{OH})_2$.
- F, HCl .
- G, $(\text{CF}_3)_2\text{AsO}\cdot\text{OH}$.
- H, $\text{CF}_3\cdot\text{AsO}(\text{OH})_2$.
- I, HNO_3 .
- J, $\text{CF}_3\cdot\text{CO}_2\text{H}$.
- K, $\text{C}_2\text{F}_5\cdot\text{CO}_2\text{H}$.
- L, $\text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$.

$\alpha^2/(1 - \alpha)$, enable a comparison of phosphorus and arsenic acids to be made (Table 3), and again reveal the marked increase in acid strength when alkyl are replaced by perfluoroalkyl groups.

In view of the well-known inaccuracies involved in calculating K from values of α for strong acids, the relative strengths of the trifluoromethyl phosphorus and arsenic acids cannot be compared accurately from the data in Table 3. Determination of the con-

ductivities of trifluoromethylphosphonic and bistrifluoromethylphosphinic acid in acetic acid solution (Tables 10 and 11) enables this comparison to be made, however. The failure to isolate anhydrous trifluoromethylphosphonous acid prevented an investigation of its strength in acetic acid solution. The specific conductivities of the acids studied in this

TABLE 3.

$\text{CF}_3\cdot\text{PO}(\text{OH})_2$	$K_1, 6.8 \times 10^{-2}$	$\text{CH}_3\cdot\text{PO}(\text{OH})_2$	$K_1, 4.2 \times 10^{-3}$	}	H_2PO_4	$K_1, 7.5 \times 10^{-3}$
	$K_2, 1.2 \times 10^{-4}$		$K_2, 1.8 \times 10^{-3}$			
$(\text{CF}_3)_2\text{PO}\cdot\text{OH}$	$K > 10^{-1}$	$(\text{CH}_3)_2\text{PO}\cdot\text{OH}$	$K, 8.3 \times 10^{-4}$			$K_3, 1.1 \times 10^{-12}$
$\text{CF}_3\cdot\text{P}(\text{OH})_2$	$K, 9.8 \times 10^{-2}$	$\text{CH}_3\cdot\text{P}(\text{OH})_2$	—	}	H_2PO_3	$K_1, 1 \times 10^{-2}$
$\text{CF}_3\cdot\text{AsO}(\text{OH})_2$	$K_1, 7.5 \times 10^{-2}$	$\text{CH}_3\cdot\text{AsO}(\text{OH})_2$	$K_1, 2.5 \times 10^{-4}$	}	H_2AsO_4	$K_1, 5 \times 10^{-3}$
	$K_2, 3 \times 10^{-6}$		$K_2, 5.7 \times 10^{-9}$			$K_2, 4 \times 10^{-5}$
$(\text{CF}_3)_2\text{AsO}\cdot\text{OH}$	$K, 3.8 \times 10^{-2}$	$(\text{CH}_3)_2\text{AsO}\cdot\text{OH}$	$K_2, 7.5 \times 10^{-7}$			$K_3, 6 \times 10^{-10}$
			$K_3, 5.6 \times 10^{-13}$			

way vary from about 1×10^{-8} for heptafluorobutyric acid (Part IX, *loc. cit.*) to 2600×10^{-8} for bistrifluoromethylphosphinic acid. The results plotted as specific conductivity against concentration (Fig. 1) give a general picture of relative acid strengths with $\text{HClO}_4 > (\text{CF}_3)_2\text{PO}(\text{OH}) > \text{HBr} > \text{H}_2\text{SO}_4 > \text{CF}_3\cdot\text{PO}(\text{OH})_2$, $\text{HCl} > (\text{CF}_3)_2\text{AsO}\cdot\text{OH} > \text{CF}_3\cdot\text{AsO}(\text{OH})_2 > \text{CF}_3\cdot\text{CO}_2\text{H}$, HNO_3 , $\text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$. Acids which are weak in acetic acid solution (HNO_3 , $\text{CF}_3\cdot\text{CO}_2\text{H}$, $\text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$) cannot be plotted conveniently in this way, and are better compared by use of a plot of equivalent conductivity against square root of concentration (Figs. 2 and 3). The curve for bistrifluoromethylphosphinic acid (Fig. 3) shows a minimum, and similar minima have been noted by Hlasko and Michalski (*Roczn. Chem.*, 1938, **18**, 220) for hydrochloric, hydrobromic, and hydriodic acids. If the values of equivalent conductivity at a particular concentration ($c = 0.49$; $10\sqrt{c} = 7$) are taken as a qualitative measure of the extent of ionisation (it being assumed that the anionic conductivities are approximately equal), the relative strengths of the acids, with $\text{CF}_3\cdot\text{CO}_2\text{H}$, HNO_3 , and $\text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$ being taken as unity, are shown in Table 4.

TABLE 4. *Relative strengths of acids.*

HClO_4	360	$\text{CF}_3\cdot\text{PO}(\text{OH})_2$	} 9	$\text{CF}_3\cdot\text{CO}_2\text{H}$	} 1
$(\text{CF}_3)_2\text{PO}(\text{OH})$	250	HCl		HNO_3	
HBr	180	$(\text{CF}_3)_2\text{AsO}\cdot\text{OH}$	3.5	$\text{C}_3\text{F}_7\cdot\text{CO}_2\text{H}$	
H_2SO_4	32	$\text{CF}_3\cdot\text{AsO}(\text{OH})_2$	2.5		

The difference between trifluoromethylarsonic acid and bistrifluoromethylarsinic acid (Part IX, *loc. cit.*) is much less than that between the corresponding phosphorus acids (Fig. 1). Bistrifluoromethylphosphinic acid is the strongest acid of phosphorus and, as shown in Fig. 1, is one of the strongest known acids.

EXPERIMENTAL

The general techniques used were the same as described in earlier papers.

Bistrifluoromethylphosphinic Acid.—(a) *Bistrifluoromethylphosphorus trichloride.* Chloro-bistrifluoromethylphosphine (13.4 g., 0.065 mole; prepared as described in Part VII) and a deficit of chlorine (4.0 g., 0.056 mole) in a sealed tube were warmed slowly from -80° to room temperature. The vigorous exothermic reaction was controlled by external cooling. After being kept for 48 hr., the products were distilled initially *in vacuo* and without contact with mercury, finally in a conventional distillation apparatus in an atmosphere of nitrogen, to give *bistrifluoromethylphosphorus trichloride* (13.8 g., 75%), b. p. $82^\circ/355$ mm. (Found: Cl, 38.1. $\text{C}_2\text{Cl}_3\text{F}_6\text{P}$ requires Cl, 38.6%). Its b. p., calculated by extrapolation of the vapour-pressure curve measured over a short temperature range, is *ca.* $107^\circ/760$ mm. The colourless liquid fumes slightly in air and has an odour like that of phosphorus pentachloride. Reaction of bistrifluoromethylphosphorus trichloride (0.2607 g.) with an excess of 15% aqueous sodium hydroxide (10 ml.) for 48 hr. gave fluoroform (0.066 g.); this corresponds to the loss of one trifluoromethyl group as fluoroform (Found: CF_3 , 25.0. $\text{C}_2\text{Cl}_3\text{F}_6\text{P}$ requires CF_3 , 50.1%). The infrared spectrum of bistrifluoromethylphosphorus trichloride (C.S. No. 149) shows strong C-F stretching vibrations at 8.47 and 8.73 μ .

(b) *Silver bistrifluoromethylphosphinate.* Bistrifluoromethylphosphorus trichloride (1.61 g.) and water (5 ml.) reacted immediately, and after 12 hr., examination of the volatile material showed that fluoroform was absent. Freeze-drying of the aqueous solution left no residue,

showing that the product is volatile in water vapour. Silver oxide (5 g.) was added slowly to the stirred condensate and after 12 hr. the solution was filtered from silver chloride and the excess of oxide. Freeze-drying of the solution gave a white solid which was dried (P_2O_5) *in vacuo* for 24 hr. then recrystallised from carbon tetrachloride-ether to give *silver bistrifluoromethylphosphinate* (1.7 g., 95%) [Found: CF_3 (as fluoroform), 22.6; Ag, 35.2. $C_2O_2F_6PAg$ requires CF_3 , 44.7; Ag, 35.0%]. Silver was determined as silver chloride and CF_3 as fluoroform by hydrolysis with an excess of aqueous sodium hydroxide; only one of the two CF_3 groups is removed under these conditions.

(c) *Isolation of bistrifluoromethylphosphinic acid.* Silver bistrifluoromethylphosphinate (9.0 g.) and concentrated sulphuric acid (5 ml.) were mixed in the bulb of a distillation apparatus and slowly heated in a nitrogen atmosphere. Two layers were formed: the lower was a solution of silver sulphate in sulphuric acid, and the upper layer distilled on rise of temperature to give *bistrifluoromethylphosphinic acid* (5.6 g., 95%), b. p. 137–138°/238 mm., 182°/760 mm. [Found: CF_3 (as fluoroform), 33.9%; equiv., 205. $C_2HO_2F_6P$ requires CF_3 , 68.3%; equiv., 202]. Only one of the CF_3 groups was lost as fluoroform on hydrolysis with 15% aqueous sodium hydroxide. The equivalent weight was determined by pH titration of 0.01M-acid (10.0 ml.) against 0.1N-sodium hydroxide solution. The point of inflection was *ca.* pH 6.5, and above pH 8.7 decomposition with liberation of fluoroform and a decrease in pH became apparent.

(d) *Anilinium bistrifluoromethylphosphinate.* To the acid (0.29 g.), dissolved in water (2.5 ml.), was added aniline (0.15 g.), and the mixture was boiled to give a clear solution which deposited crystals on cooling. Recrystallisation from benzene gave *anilinium bistrifluoromethylphosphinate* (0.22 g.) (Found: C, 32.8; H, 3.1; N, 4.8%; equiv., 297. $C_8H_8O_2NF_6P$ requires C, 32.6; H, 2.7; N, 4.8%; equiv., 295). The equivalent weight was determined by direct titration with 0.0878N-sodium hydroxide solution.

(e) *Preparation from tris(trifluoromethyl)phosphorus dichloride.* The chloro-compound was prepared by the method described in Part VII. Tris(trifluoromethyl)phosphorus dichloride (1.235 g.) and water (3 ml.) underwent an exothermic reaction to give, after 48 hr., fluoroform (0.272 g., 33%) and an aqueous solution which was completely volatile when subjected to the freeze-drying procedure. The condensate was treated with an excess of freshly-prepared silver oxide (3 g.) and after 6 hr. was filtered and freeze-dried to give silver bistrifluoromethylphosphinate (1.18 g., 95%) (Found: Ag, 35.1. Calc. for $C_2O_2F_6PAg$: Ag, 35.0%) identified by means of its infrared spectrum.

Reaction of tris(trifluoromethyl)phosphorus dichloride (0.340 g.) with 10% aqueous sodium hydroxide (10 ml.) for 48 hr. gave fluoroform (0.154 g., 67%) and an aqueous solution which, when freeze-dried, left a residue of disodium trifluoromethylphosphonate, identified by means of its infrared spectrum.

Trifluoromethylphosphonic Acid.—(a) *Potassium salts.* Trifluoromethylphosphonic acid (4.105 g.), purified by sublimation *in vacuo* and dried *in vacuo* (over P_2O_5) for 6 hr., was dissolved in water (20 ml.) and neutralised with 5% potassium carbonate solution (3.78 g. of K_2CO_3 required). A pH meter accurate to ± 0.02 unit was used to determine the end-point. The solution was freeze-dried (2 days) to give *dipotassium trifluoromethylphosphonate* (6.1 g., 97%) (Found: K, 34.6. $CO_3F_3K_2P$ requires K, 34.5%).

Trifluoromethylphosphonic acid (1.067 g.) was dissolved in water (20 ml.) and a solution of potassium carbonate (0.4917 g.) in water (10 ml.) was added with stirring. Freeze-drying (24 hr.) gave *monopotassium trifluoromethylphosphonate* (1.297 g., 95%) (Found: K, 20.8. CHO_3F_3KP requires K, 20.8%).

(b) *Aniline salts.* Aniline (0.17 g.), dissolved in ethanol (1 ml.), was slowly added to trifluoromethylphosphonic acid (0.29 g.). The mixture was heated (100°) until solution was complete, and after cooling, *monoanilinium trifluoromethylphosphonate* (0.3 g.) (Found: C, 34.1; H, 4.0; N, 5.5. $C_7H_7O_3NF_3P$ requires C, 34.5; H, 3.7; N, 5.7%) was removed by filtration and recrystallised from ethanol.

Similar reaction of aniline (0.45 g.), ethanol (2 ml.), and trifluoromethylphosphonic acid (0.36 g.) gave *dianilinium trifluoromethylphosphonate* (0.5 g.) (Found: C, 46.2; H, 5.3; N, 8.6. $C_{13}H_{16}O_3N_2F_3P$ requires C, 46.4; H, 4.8; N, 8.3%), recrystallised from ethanol.

The aniline salts decomposed without melting when heated, and were therefore characterised by their infrared spectra.

(c) *Preparation.* The method described in Part X was used, with the improvement that the crude mixture of iodobistrifluoromethylphosphine and di-iodotrifluoromethylphosphine obtained by distillation of the reaction products of trifluoroiodomethane and phosphorus was used directly. In a typical experiment, the mixture (20 g.) was added to water (50 ml.), and the two phases were

stirred for 2 hr. During this period the two layers became homogeneous and fluoroform was liberated during the exothermic reaction. When cold, the solution was treated with unstabilised 100-vol. hydrogen peroxide, added dropwise with constant stirring until iodine was no longer liberated and the exothermic reaction ceased. After filtration, the solution was freeze-dried (4 days) to give crude trifluoromethylphosphonic acid, which was purified by sublimation (6.1 g.) (Found: equiv., 75.4. Calc. for $\text{CH}_2\text{O}_3\text{F}_3\text{P}$: equiv., 75.0). Since the acid is very hygroscopic it was manipulated in a dry box and was dried *in vacuo* for 6 hr. before use.

Trifluoromethylphosphonous Acid.—(a) *Potassium salt.* Tris(trifluoromethyl)phosphine (4.5 g., 0.019 mole) and 0.147N-aqueous potassium hydroxide (100 ml., 0.015 mole) in a 250-ml. Carius tube were shaken vigorously in a vibro-shaker for 24 hr. Fluoroform and unreacted tris(trifluoromethyl)phosphine (21%) were removed, and the residual aqueous solution was freeze-dried (48 hr.) to give *potassium trifluoromethylphosphonite* (2.5 g., 98%) (Found: K, 22.9; CF_3 , 40.0. $\text{CHO}_2\text{F}_3\text{KP}$ requires K, 22.8; CF_3 , 40.1%). Vigorous shaking is essential, since without rapid hydrolysis some of the potassium trifluoromethylphosphonite is hydrolysed to fluoroform by the excess of potassium hydroxide present in the early stages of the reaction, and potassium phosphite contaminates the product. Potassium was determined as chloroplatinate after a preliminary evaporation of the salt to dryness with nitric acid to prevent the reduction of the chloroplatinic acid, and CF_3 was determined as fluoroform by reaction with an excess of aqueous sodium hydroxide.

(b) *Aqueous solutions of the acid.* The method described in Part X was applied on a larger scale. In a typical experiment, tris(trifluoromethyl)phosphine (6.0 g., 0.025 mole) and 1.011N-sodium hydroxide solution (24.9 ml., 0.025 mole) were shaken in a 150-ml. sealed tube for 48 hr. Fractionation of the volatile products gave fluoroform (3.5 g., 0.05 mole, 67%). Sulphuric acid (1 ml.) was added to the aqueous solution, and the acidic solution was freeze-dried. The condensate was again freeze-dried to remove final traces of sodium sulphate, diluted to 250 ml., and standardised by titration with carbonate-free sodium hydroxide solution.

Slightly impure solutions of trifluoromethylphosphonous acid were prepared by aqueous hydrolysis of di-iodotrifluoromethylphosphine followed by the addition of sufficient sodium carbonate to neutralise the hydriodic acid present, and freeze-drying. The distillate was aqueous trifluoromethylphosphonous acid contaminated by a small amount of iodide. In a typical experiment di-iodotrifluoromethylphosphine (2.6 g.) and water (5 ml.) were kept until the solution became homogeneous (2 hr.). Potassium carbonate (1.05 g.) was added and the solution freeze-dried to leave a residue of potassium iodide and give a distillate of trifluoromethylphosphonous acid containing a small amount of hydriodic acid.

(c) *Reducing properties of trifluoromethylphosphonous acid.* An aqueous solution of this acid, prepared from pure potassium salt as described above, was 0.0655N as determined by titration with 0.113N-sodium hydroxide with use of a pH meter to determine the end-point. Its reducing power was tested as follows:

(i) *With iodine solution.* Trifluoromethylphosphonous acid (10 ml. of 0.0655N) was made slightly alkaline by adding sodium hydrogen carbonate (1 g.) and kept at room temperature with 0.12N-iodine solution (20 ml.) for 18 hr. Back-titration with 0.1N-sodium thiosulphate solution (23.9 ml.) showed that no reaction had taken place.

(ii) *With mercuric chloride.* A solution of the acid (20 ml.) was buffered with sodium acetate (2 g.) and glacial acetic acid (2 ml.), and to it was added saturated mercuric chloride solution (20 ml.). Mercurous chloride was not produced at room temperature, but was deposited at 60°; the reaction was 93% complete after 4 hr.

(iii) *With potassium iodate.* A solution of the acid (10 ml.), 0.2213N-potassium iodate (30 ml.), and 5N-sulphuric acid (5 ml.) was kept overnight. Addition of an excess of potassium iodide (2 g.) and titration with 0.1235N-sodium thiosulphate solution (10.25 ml.) showed that 97% of the trifluoromethylphosphonous acid had been oxidised.

(iv) *With ceric sulphate.* Trifluoromethylphosphonous acid (10 ml. of 0.0655N) did not react during 5 min. at 20° with an excess of 0.1465N-ceric sulphate solution (20 ml.), but after being kept at 50° for 5 min., and left to cool (2 hr.), back-titration with 0.0901N-ferrous sulphate solution (19.7 ml.) (ferrous phenanthroline as indicator) showed that 89% had been oxidised to trifluoromethylphosphonic acid. A similar mixture, kept overnight at 20°, warmed to 50° (5 min.), cooled (2 hr.), then titrated, required 19.2 ml. of the ferrous sulphate solution, indicating that 92% of the acid had been oxidised.

(v) *With potassium permanganate.* An excess of 0.101N-potassium permanganate solution (20 ml.) was added to trifluoromethylphosphonous acid solution (10 ml.) containing an excess of 5N-sulphuric acid (20 ml.). The mixture was heated to 60°, cooled, left for 2 hr., then back-

titrated with 0.0901N-ferrous sulphate (8.07 ml.); 99% of the trifluoromethylphosphonous acid had been oxidised.

The normality of trifluoromethylphosphonous acid for an oxidation titration is twice that for a base titration [cf. $\text{CF}_3\cdot\text{PHO}(\text{OH}) + \text{O} \longrightarrow \text{CF}_3\cdot\text{PO}(\text{OH})_2$; $\text{CF}_3\cdot\text{PHO}(\text{OH}) + \text{NaOH} \longrightarrow \text{CF}_3\text{PHO}(\text{ONa})$].

(d) *Attempted preparation of the anhydrous acid.* Potassium trifluoromethylphosphonite (0.5 g.) heated (60°) with concentrated sulphuric acid (1 ml.) was oxidised to trifluoromethylphosphonic acid; sulphur dioxide was produced.

When potassium trifluoromethylphosphonite (0.5 g.), phosphoric acid (1 g.), and phosphoric anhydride (1 g.) were heated gently with a micro-burner, trifluoromethylphosphine (0.23 g.) (Found: *M*, 101. Calc. for $\text{CH}_2\text{F}_3\text{P}$: *M*, 102) was the only volatile product.

(e) *Hydrolysis of trifluoromethylphosphonous acid.* A solution of the acid (20 ml. of 0.0655N), heated in a sealed tube at 100° (24 hr.), gave fluoroform (0.885 g., 97%) and phosphorous acid (98%, by titration with iodine solution).

The hydrolysis in presence of hydriodic acid followed a similar course. Di-iodotrifluoromethylphosphine (2.6 g.) and water (10 ml.) were heated at 140° for 24 hr. to give fluoroform (0.50 g., 98%) and phosphorous acid (0.60 g., 99%).

In a third experiment, di-iodotrifluoromethylphosphine (4.68 g.) and water (5 ml.), heated at 140° (24 hr.) in an 80-ml. tube, gave fluoroform (0.8525 g., 92%), trifluoromethylphosphine (0.0375 g., 8%), and phosphorous acid (0.9716 g., 90%). The volatile products were identified by infrared spectroscopy in the usual way.

Disproportionation of Trifluoromethylphosphonous Acid.—That the acid disproportionates into trifluoromethylphosphine and trifluoromethylphosphonic acid when prepared in concentrated aqueous solution is shown by the following experiments on the hydrolysis of di-iodotrifluoromethylphosphine.

(a) The di-iodide (2.6 g., 0.007 mole) and water (4.9 g., 0.27 mole) were kept under a nitrogen atmosphere until the solution was homogeneous (2 hr.). When the liquid was frozen and freeze-dried it was found to be completely volatile, *i.e.*, contained only trifluoromethylphosphonous acid and hydriodic acid.

(b) The reaction product from di-iodotrifluoromethylphosphine (5.2 g., 0.015 mole) and water (3.8 g., 0.21 mole) was completely volatile when freeze-dried.

(c) Di-iodotrifluoromethylphosphine (25.3 g., 0.071 mole) and water (9.8 g., 0.54 mole) were kept for 12 hr. so that the two layers initially present merged into one. The solution was freeze-dried (14 days) to give trifluoromethylphosphonic acid [3.2 g., 45% of theory expected from the equation $3\text{CF}_3\cdot\text{P}(\text{OH})_2 \longrightarrow 2\text{CF}_3\cdot\text{PO}(\text{OH})_2 + \text{CF}_3\cdot\text{PH}_2$] as a white solid residue, trifluoromethylphosphine (1.01 g., 42% of theory expected from the last equation) (Found: *M*, 103. Calc. for $\text{CH}_2\text{F}_3\text{P}$: *M*, 102), and a condensate containing trifluoromethylphosphonous acid. The trifluoromethylphosphine was purified by treatment with water (20 ml.) to remove contaminating hydriodic acid, followed by fractionation *in vacuo*; it was identified by means of its infrared spectrum. Trifluoromethylphosphonic acid was purified by sublimation *in vacuo*, leaving no residue, and titration with sodium hydroxide solution revealed two points of inflection and an equivalent weight of 76.5 (Calc. for $\text{CH}_2\text{O}_3\text{F}_3\text{P}$: equiv., 75) (cf. Part X). The acid was identified by preparation of its monopotassium salt by reaction of potassium carbonate (0.105 g.) with a solution of the acid (0.23 g.) in water (5 ml.) followed by evaporation to dryness *in vacuo* (Found: *K*, 20.7. Calc. for $\text{CHO}_3\text{F}_3\text{KP}$: *K*, 20.8%). The infrared spectrum was identical with that of known monopotassium trifluoromethylphosphonate. The monoanilinium salt (0.21 g.) was prepared from the acid (0.264 g.), aniline (0.15 g.), and ethanol (1 ml.), and recrystallised from ethanol (Found: *C*, 34.2; *H*, 3.3; *N*, 5.7. Calc. for $\text{C}_7\text{H}_7\text{O}_3\text{NF}_3\text{P}$: *C*, 34.5; *H*, 3.7; *N*, 5.8%); it had an infrared spectrum identical with that of an authentic sample. Final confirmation was given by the preparation of the dianiline salt from the acid (0.32 g.), aniline (0.45 g.), and ethanol (2 ml.). The salt (0.40 g.) (Found: *C*, 46.4; *H*, 4.6; *N*, 8.2. Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{N}_2\text{F}_3\text{P}$: *C*, 46.4; *H*, 4.8; *N*, 8.3%) was recrystallised from ethanol, and was spectroscopically identical with known dianilinium trifluoromethylphosphonate. That the trifluoromethylphosphonic acid so prepared was uncontaminated by trifluoromethylphosphonous acid was shown by its failure to liberate fluoroform when treated with 15% sodium hydroxide for 48 hr.

Conductivities in Aqueous Solution.—Solutions were made up by weight, in conductivity water ($\kappa < 1 \times 10^{-6}$), and were diluted by weight. All measurements were made at $25^\circ \pm 0.02^\circ$ in cells of conventional design with sealed-in platinised platinum electrodes. The cells had cell constants 13.29 (A), 4.359 (later 4.347) (B), and 0.05338 (later 0.05112) (C). Resistances

were measured by a Wheatstone bridge circuit with a cathode-ray oscilloscope as null-point detector (Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544). Auxiliary resistances were used in parallel when the cell resistance became greater than 10,000 ohms, and in series when the resistance was less than 500 ohms. In the following Tables, c = concentration (moles/l.), κ = specific conductivity, λ_c = molecular conductivity, $\lambda_{\text{corr.}}$ = corrected molecular conductivity, calculated from the equation $\lambda_c = \lambda_{\text{corr.}} - (A + B\lambda_{\text{corr.}})\sqrt{c}$ with $A = 60.21$, $B = 0.2289$.

In Table 1, α ($= \lambda_c/\lambda_x$) was calculated from the equation $\lambda_x = \lambda_{\text{cc}} - (A + B\lambda_{\text{cc}})\sqrt{c\lambda_c/\lambda_x}$. Provisional values of λ_x were obtained for different concentrations, the quantity λ_x under the square-root sign being replaced by λ_{cc} . The approximate results for λ_x were then used in the $\sqrt{c\lambda_c/\lambda_x}$ term and a more accurate value of λ_x computed; this was continued until λ_x remained constant, and α was then calculated.

The calculation of ionisation constant K from α cannot lead to accurate values for K , particularly since for strong acids, with $\alpha \sim 1$, a small change in α makes a very large change in K .

(a) *Trifluoromethylphosphonic acid*. This was prepared from the iodotrifluoromethylphosphine (Part X) and was purified by sublimation *in vacuo*. The results are shown in Table 5.

TABLE 5. $\text{CF}_3\cdot\text{PO}(\text{OH})_2$.

10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	Cell	10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	Cell
592.3	24.33	206.7	349.1	A	34.35	5.850	12.95	377.1	B
286.6	16.93	102.3	356.6	A	33.47	5.785	12.56	375.3	B
130.2	11.41	47.35	363.6	A	16.26	4.032	6.262	385.1	B
70.25	8.381	26.02	370.5	A	7.394	2.719	2.961	400.4	B
60.27	7.763	22.39	371.5	B					

(b) *Bistrifluoromethylphosphinic acid*. The acid, prepared as described above, was freshly distilled before use, and gave the results shown in Table 6.

TABLE 6. $(\text{CF}_3)_2\text{PO}\cdot\text{OH}$.

10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	$\lambda_{\text{corr.}}$	Cell	10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	$\lambda_{\text{corr.}}$	Cell
278.9	16.70	100.9	362.0	386.6	A	42.59	6.525	16.03	376.5	386.3	B
131.9	11.48	48.76	369.6	386.6	A	16.54	4.068	6.277	379.5	385.5	B
113.6	10.65	42.13	370.9	386.8	A	9.757	3.123	3.717	381.0	385.8	B
73.75	8.590	27.51	373.0	386.3	A, B	5.294	2.301	2.624	382.3	385.8	B

λ_{∞} (graphical) = 385.7.

(c) *Trifluoromethylphosphonous acid*. Since this acid cannot be isolated in the anhydrous state, a carefully purified aqueous solution (see p. 571) was standardised by pH titration against aqueous sodium hydroxide; dilutions from the standardised solution were made by weight. The results are given in Table 7.

TABLE 7. $\text{CF}_3\cdot\text{P}(\text{OH})_2$.

10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	Cell	10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	Cell
351.5	18.75	121.4	345.3	A	24.58	4.958	8.974	365.1	B
165.6	12.86	58.15	351.1	A	13.57	3.684	4.996	368.1	B
99.82	9.996	35.44	355.0	A	11.61	3.408	4.295	369.8	B
68.16	8.254	24.31	357.1	A	4.342	2.084	1.624	373.9	B
54.29	7.367	19.54	359.9	A, B					

λ_{∞} (graphical) = 379.0.

(d) *Potassium trifluoromethylphosphonates*. The results are given in Table 8 and 9.

TABLE 8. $\text{CF}_3\cdot\text{PO}(\text{OH})(\text{OK})$.					TABLE 9. $\text{CF}_3\cdot\text{PO}(\text{OK})_2$.				
10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	Cell	10^4c	$10^2\sqrt{c}$	$10^4\kappa$	λ_c	Cell
476.4	21.83	51.3	107.6	A	521.1	22.82	98.45	188.9	B
192.1	13.86	22.95	119.5	A	264.0	16.25	53.01	200.7	B
104.7	10.23	13.51	129.0	A, B	92.70	9.629	20.12	217.0	B
58.51	7.650	8.547	146.1	B	45.02	6.710	10.29	228.1	B
48.19	6.940	7.071	145.6	B	39.14	6.258	8.973	229.2	B
29.07	5.392	4.733	162.9	B	20.25	4.500	4.807	237.4	B
15.31	3.912	2.671	174.4	B	9.716	3.118	2.377	244.6	B
11.11	3.333	2.164	194.8	B	4.215	2.053	1.065	252.6*	B
4.861	2.205	1.127	231.9	B	1.933	1.391	0.5052	261.3*	B
2.490	1.578	0.6745	270.9	B					

λ_{∞} (graphical) = 256.0.

* These points are slightly higher than expected, and may indicate slight hydrolysis of the salt; the second dissociation constant of $\text{CF}_3\cdot\text{PO}(\text{OH})_2$ is 1.2×10^{-4} .

Conductivities in Acetic Acid Solution.—"AnalaR" acetic acid was further purified (Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, **56**, 1007) and had κ $1.5\text{--}1.8 \times 10^{-8}$. The cells and apparatus were the same as used for the aqueous solutions.

The results are given in Tables 10 and 11.

TABLE 10. $\text{CF}_3\cdot\text{PO}(\text{OH})_2$ in acetic acid.

10^4c	$10^2\sqrt{c}$	$10^3\kappa$	$10^2\lambda_c$	Cell	10^4c	$10^2\sqrt{c}$	$10^3\kappa$	$10^2\lambda_c$	Cell
280.8	16.75	31.48	1.121	C	51.56	7.180	10.50	2.036	C
193.5	13.91	25.26	1.305	C	16.99	4.122	5.641	3.320	C
85.65	9.253	14.40	1.682	C					

TABLE 11. $(\text{CF}_3)_2\text{PO}\cdot\text{OH}$ in acetic acid.

10^4c	$10^2\sqrt{c}$	$10^3\kappa$	λ_c	Cell	10^4c	$10^2\sqrt{c}$	$10^3\kappa$	λ_c	Cell
539.2	23.21	25.73	0.4772	C	56.67	7.528	2.883	0.5086	C
308.7	17.57	12.59	0.4079	C	45.40	6.738	2.519	0.5546	C
294.4	17.16	12.69	0.4310	C	25.13	5.013	1.726	0.6869	C
127.6	11.30	5.338	0.4181	C	12.26	3.501	1.177	0.9601	C
111.7	10.57	4.899	0.4385	C					

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