

CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE
UNIVERSITY OF TULSA, TULSA 4, OKLAHOMA, AND THE UNIVERSITY OF OKLAHOMA, NORMAN, OKLAHOMA

Kinetics of Hydrolysis of Fluorophosphates.

I. Monofluorophosphoric Acid¹

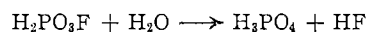
By L. N. DEVONSHIRE AND H. H. ROWLEY

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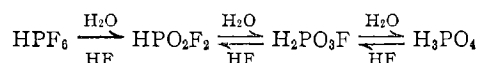
Pseudo first-order reaction rate constants for the hydrolysis of $\text{H}_2\text{PO}_3\text{F}$ have been determined as a function of pH. The pH dependence indicates slow rates of hydrolysis for PO_3F^{2-} and HPO_3F^- . In acidic solution the kinetics are described by the expression $-dC/dt = k[\text{H}_2\text{PO}_3\text{F}][\text{H}^+]$, where C is the total formal concentration of all monofluorophosphate species at time t . The Arrhenius energy of activation is 16.3 ± 1 kcal./mole. Finally, a mechanism is proposed which involves the intermediate formation of a protonated complex,

The relative rates of hydrolysis of the fluorophosphoric acids in dilute solution are well known,^{2,3} and the equilibria involved in concentrated solution have been quantitatively investigated.^{4,5} However, except for a single run,⁶ a study of the kinetics of hydrolysis of this system in dilute solution has not been reported.

As part of a program of comparing the kinetics of hydrolysis of the fluorophosphates, this paper describes a study of the reaction



This reaction is the final step in the hexafluorophosphate to orthophosphate hydrolysis sequence⁷



Reports on the kinetics of hydrolysis of hexafluorophosphate and difluorophosphate are in preparation.

Experimental

Compounds.—Analyzed experimental samples reported as 96% $\text{Na}_2\text{PO}_3\text{F}$ were furnished by Dr. Wayne E. White of the Ozark-Mahoning Co. These samples were prepared by fusing stoichiometric quantities of anhydrous sodium

trimetaphosphate and sodium fluoride in platinum at 800° .⁸

Pure silver monofluorophosphate, $\text{Ag}_2\text{PO}_3\text{F}$, was prepared by the method of Lange.⁶ This salt was used in the ion-exchange experiments.

Sodium perchlorate solution was prepared by neutralization of standard perchloric acid with carbonate-free sodium hydroxide solution.

All other chemicals were commercially available and of reagent quality.

Kinetic Procedure.—Solutions of reactants were preheated in stoppered polyethylene bottles in water baths which were thermostatically controlled to $\pm 0.1^\circ$. After reaching thermal equilibrium, the solutions were quickly mixed. Using 10 or 25 ml. pipets, aliquots for analysis were withdrawn at known times. Reactions in the aliquots were quenched by dilution in approximately 300 ml. of solution containing the previously measured quantity of standard acid or base required for approximate neutralization.

Analytical Methods.—Aliquots were analyzed for orthophosphate or for increase in titratable acid, or both. Orthophosphate was determined by the modified Volhard⁹ method. Increase in acidity was determined by titration to the thymolsulfonphthalein end point using standard sodium hydroxide or perchloric acid.

Measurements of pH were made using a glass-calomel electrode system with a Beckman Zeromatic pH meter standardized using certified Coleman buffers. Erratic glass electrode behavior in HF solutions invalidated most pH data.

Ion-Exchange Experiments.—Solutions of $\text{H}_2\text{PO}_3\text{F}$ were prepared by passing solutions of $\text{Na}_2\text{PO}_3\text{F}$ or $\text{Ag}_2\text{PO}_3\text{F}$ through the acid form of a Nalcite-HCR cation-exchange resin column. Only a single run using this method of preparation is reported, however, since at higher concentrations appreciable hydrolysis took place before the solutions could be brought to constant temperature.

Spectrophotometric Study.—Attempts to locate a characteristic absorption peak which could be used in following the course of the reaction at the concentrations reported were unsuccessful. These measurements were

(1) This investigation was supported, in part, by the Ozark-Mahoning Co., Tulsa, Okla.

(2) W. Lange, "Fluorine Chemistry," Vol. I, J. H. Simons (Ed.), Academic Press, New York, N. Y., 1950, Chap. 3, pp. 125-188.

(3) J. R. Van Wazer, "Phosphorus and Its Compounds. I: Chemistry," Interscience, New York, N. Y., 1958, Chap. 13, pp. 801-820.

(4) W. Lange, *Ber.*, **62B**, 1084 (1929); *Z. anorg. allgem. Chem.*, **214**, 44 (1933).

(5) D. P. Ames, S. Ohashi, C. F. Callis, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **81**, 6350 (1959).

(6) W. Lange, *Ber.*, **62**, 793 (1929).

(7) W. Lange and R. Livingston, *J. Am. Chem. Soc.*, **69**, 1073 (1947).

(8) C. F. Hill and L. F. Audrieth, "Inorganic Syntheses, III," Maple Press Co., New York, N. Y., 1950, p. 111.

(9) J. Volhard, *J. prakt. Chem.*, **117**, 217 (1874).

made from 220 to 350 $m\mu$ using a Beckman Model DU spectrophotometer.

Titration Curves.—Titration curves were obtained by plotting measured pH values *vs.* ml. of standard acid added during the titration of standard $\text{Na}_2\text{PO}_3\text{F}$ solutions. These titration curves were used in estimating the primary and secondary ionization constants for $\text{H}_2\text{PO}_3\text{F}$. A report of this work was submitted to Van Wazer and has been reported in his book.³ Approximate primary and secondary ionization constants for $\text{H}_2\text{PO}_3\text{F}$ are reported as $K_1 = 0.3$ and $K_2 = 1.6 \times 10^{-5}$. As will be seen, an assumed value for K_1 of 0.80 rather than 0.3 is more satisfactory in treating the kinetics data. This apparent discrepancy is reconciled by the fact that pH measurements are of activities whereas the assumed value is based upon concentration. Because the similarity of monofluorophosphates to sulfates is well known,² and because the mean activity coefficient for 0.05 M H_2SO_4 at 40° is reported¹⁰ as 0.301, this reconciliation appears to be a reasonable one.

Results

The analytical data were used for calculating the concentration of unhydrolyzed monofluorophosphate in each aliquot. These calculations were based on the stoichiometry of the reaction under investigation. The apparent fraction, C/C_0 , where C_0 is the initial formal concentration of sodium monofluorophosphate and C is the formal concentration of unhydrolyzed monofluorophosphate at time t , was calculated for each aliquot. For each run the calculated C/C_0 values were plotted *vs.* t on semilogarithm graph paper and the best-fitting line was drawn. Pseudo first-order reaction rate constants, k_{obs} , were calculated by standard procedure from the slopes of these lines. Calculated values of k_{obs} as functions of initial concentrations of reactants at 27, 40, and 80° are presented in Tables I, II, and III.

Treatment of Data.—Referring to the data in Table I, for example, it is seen that the values of k_{obs} decrease with decreasing concentration of perchloric acid and become very small as the perchloric acid concentration approaches the monofluorophosphate concentration. It appears, then, that the acid in excess of that required to convert PO_3F^{2-} into HPO_3F^- functions to catalyze the hydrolysis. Since the primary ionization constant for $\text{H}_2\text{PO}_3\text{F}$, $K_1 = 0.3$, is rather large while the secondary ionization constant, $K_2 = 1.6 \times 10^{-5}$, is quite small, very little error is introduced by assuming that the $[\text{H}^+]$ is equal to the difference between the per-

(10) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).

TABLE I
RATES OF HYDROLYSIS OF 0.048 f $\text{Na}_2\text{PO}_3\text{F}$ AS A FUNCTION OF PERCHLORIC ACID CONCENTRATION AT 40°

$[\text{HClO}_4]$	pH	k_{obs} (min.^{-1}) $\times 10^2$	k
0.0873	1.50	0.396	0.218
.100	1.35	.660	.208
.185		4.94	.248
.199		5.77	.242
.220		7.30	.242
.249		9.93	.248
.280		13.6	.260
.374		21.6	.230
.599		57.7	.257
.796		88.9	.247
1.000		128	.248
1.200		161	.238

Av. .240 Av. deviation
 ± 0.012

$$k = k_{\text{obs}} \left[\frac{[\text{H}^+] + K_1}{[\text{H}^+]^2} \right]$$

TABLE II
RATES OF HYDROLYSIS OF $\text{Na}_2\text{PO}_3\text{F}$ AS A FUNCTION OF PERCHLORIC ACID CONCENTRATION AT 80°

$[\text{Na}_2\text{PO}_3\text{F}]$	$[\text{HClO}_4]$	k_{obs} (min.^{-1}) $\times 10^2$	k
0.1000	0.1000	0.02	
.048	.100	16.6	4.95
.048	.121	31.8	4.85
.048	.139	48.1	4.77
.048	.161	66.6	4.25
.048	.186	106	4.54
.048	.194	117	4.50
.087	.180	42.7	4.42
.080	.160	31.4	4.33
.072	.150	32.0	4.62

Av. 4.59 Av. deviation
 ± 0.19

0.048	$0.100 + 0.2 f \text{ NaClO}_4$	16.2	
.048	$.100 + .4 f \text{ NaClO}_4$	15.8	
.048	$.100 + .6 f \text{ NaClO}_4$	15.5	
.048	$.100 + .8 f \text{ NaClO}_4$	15.2	
(0.0221 f $\text{H}_2\text{PO}_3\text{F}$ from ion exchange)		2.54	4.36

$$k = k_{\text{obs}} \left[\frac{[\text{H}^+] + K_1}{[\text{H}^+]^2} \right]$$

chloric acid concentration and the monofluorophosphate concentration. Figure 1 is a plot of $\log k_{\text{obs}}$ *vs.* $\log [\text{H}^+]$ for the 0.048 f monofluorophosphate solutions at 40 and 80° where the $[\text{H}^+]$ is calculated in this manner.

The slopes in Fig. 1 of both the 40 and 80° data are very nearly equal to two with significant deviations in the 40° data at the higher acidities,

TABLE III
RATES OF HYDROLYSIS OF $\text{Na}_2\text{PO}_3\text{F}$ IN CONCENTRATED
 HClO_4 AND NaOH SOLUTIONS

T , °C.	$[\text{Na}_2\text{PO}_3\text{F}]$	$[\text{HClO}_4]$	$[\text{NaOH}]$	k_{obs} (min.^{-1}) $\times 10^3$	k
27	0.050	1.20		49.5	0.073
27	.050	1.60		75.3	.074
80	.048		0.60	0.049	
40	.048		3.50	1.72	

Av. .0735

$$k = \left[\frac{[\text{H}^+] + K_1}{[\text{H}^+]^2} \right] k_{\text{obs}}$$

By assuming various kinetic expressions and attempting to fit all the data into the predictions made on the basis of these assumptions, the rate expression: $-dC/dt = k[\text{H}_2\text{PO}_3\text{F}][\text{H}^+]$, where C is the total formal concentration of all unhydrolyzed monofluorophosphate species at time t , was selected because it allows correlation of all the data. It is apparent that the rate of hydrolysis of the HPO_3F^- is very slow compared with that of $\text{H}_2\text{PO}_3\text{F}$.

One may solve for the value of $[\text{H}_2\text{PO}_3\text{F}]$ in terms of the first ionization constant, K_1 , for $\text{H}_2\text{PO}_3\text{F}$ and in terms of the total concentration of all monofluorophosphate species C , where $C = [\text{HPO}_3\text{F}^-] + [\text{H}_2\text{PO}_3\text{F}]$. If this value for $[\text{H}_2\text{PO}_3\text{F}]$ is placed in the rate expression, one obtains the relationship

$$\frac{-dC}{dt} = \frac{kC[\text{H}^+]^2}{[\text{H}^+] + K_1} = k_{\text{obs}}C$$

which predicts a first-order reaction at constant pH where $k_{\text{obs}} = \frac{k[\text{H}^+]^2}{[\text{H}^+] + K_1}$.

One then may solve for k in terms of calculated $[\text{H}^+]$, K_1 , and experimentally determined k_{obs}

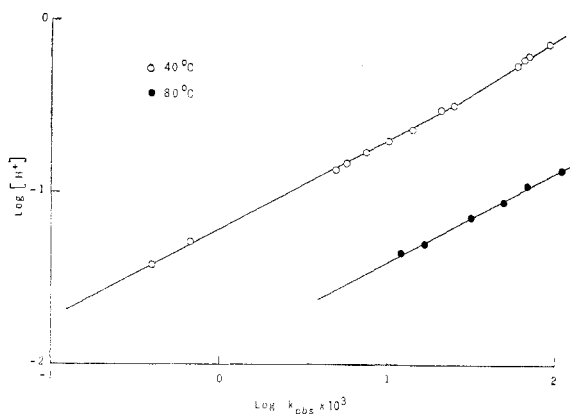


Fig. 1.—Logarithmic plot of k_{obs} (min.^{-1}) $\times 10^3$ vs. logarithm of the calculated H^+ concentration.

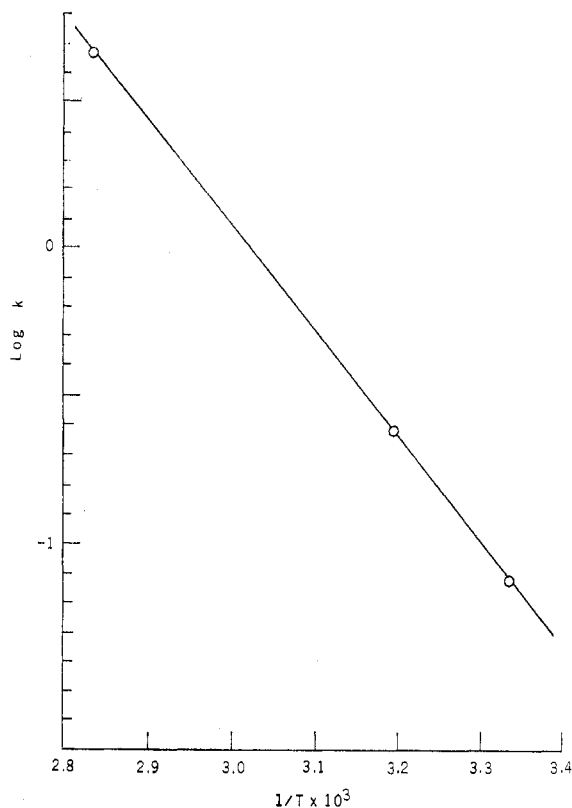


Figure 2.

values. When this is done, a value for K_1 of approximately 0.8 must be used in order to obtain constant k values when all the data are considered. Values for k calculated in this manner are tabulated in the last column of Tables I, II, and III. A k value is not reported for the first entry in Table II since the k_{obs} reported is approximate. The close agreement of the calculated k values is taken as justification for the preferred rate expression.

Salt Effect.—The data in Table II indicate that rather high NaClO_4 concentrations cause a slight decrease in k_{obs} values.

Hydrolysis in Basic Solution.—Also included in Table III are calculated k_{obs} values for the hydrolysis of 0.048 f $\text{Na}_2\text{PO}_3\text{F}$ in 0.6 f NaOH at 80° and 3.50 f NaOH at 40°. As pointed out earlier,² these data indicate that the PO_3F^{2-} ion is remarkably stable toward hydrolysis in neutral or moderately alkaline solution, but that heating in strongly alkaline solution results in rapid hydrolysis.

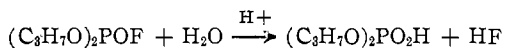
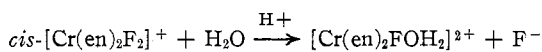
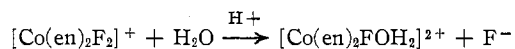
Arrhenius Activation Energy.—Figure 2 is a plot of the average values of $\log k$ as reported in Tables I, II, and III vs. $1000/T$ ($^{\circ}\text{K.}$) at temperatures of 27, 40, and 80°. The apparent Arrhenius energy of activation is 16.3 ± 1 kcal./mole.

Discussion

The rate of hydrolysis of $\text{H}_2\text{PO}_3\text{F}$ is adequately described by the expression

$$\text{rate} = k[\text{H}_2\text{PO}_3\text{F}][\text{H}^+]$$

This expression is formally similar to that for the acid-catalyzed processes¹¹⁻¹⁴



en = ethylenediamine; $\text{C}_3\text{H}_7\text{O}$ = isopropyl

Presumably due to coulombic repulsion, alkaline hydrolysis of the PO_3F^{2-} ion is extremely slow even in 0.6 *f* NaOH, whereas the alkaline hydrolysis of the other systems¹¹⁻¹⁴ which involves either positively charged or uncharged species is very rapid. The slight decrease in k_{obs} values with increasing NaClO_4 concentration, Table II,

(11) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

(12) K. R. A. Fehrmann and C. S. Garner, *ibid.*, **83**, 1276 (1961).

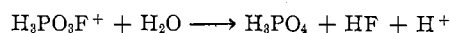
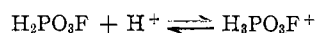
(13) W. A. Waters and C. G. de Worms, *J. Chem. Soc.*, 926 (1949).

(14) M. L. Kilpatrick and M. J. Kilpatrick, *J. Phys. and Colloid Chem.*, **53**, 1358, 1371 (1949).

may be accounted for in terms of the general increase in the extent of ionization of weak acids with increasing ionic strength or perhaps in terms of the effect of high salt concentration upon activities.

It is interesting to compare the energy of activation for the hydrolysis of the more covalent P-F bond with those for the more ionic Cr-F and Co-F bonds. They are 16.3, as determined in this study, 23, and 29 kcal./mole, respectively.¹² Basolo, *et al.*,¹¹ have discussed other examples where the lability is inversely related to the degree of ionic character.

Finally, it seems reasonable to postulate, as was done by other workers¹¹⁻¹⁴ in the analogous cases, that the acid-catalyzed hydrolysis of $\text{H}_2\text{PO}_3\text{F}$ involves a rapid acid-base pre-equilibrium, followed by slow aquation of the protonated complex as the rate-determining step



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CONTRIBUTION FROM THE CHEMICAL TECHNOLOGY DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE¹

Hydrolysis of Uranium Carbides between 25 and 100°.

I. Uranium Monocarbide

By MILDRED J. BRADLEY AND LESLIE M. FERRIS

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High-purity uranium monocarbide, when allowed to react with water at temperatures between 25 and 99°, yielded a gelatinous, hydrous, tetravalent uranium oxide and a gas (93 ml. (STP) per gram of UC hydrolyzed) consisting of 86 vol. % methane, 11 vol. % hydrogen, 1.8 vol. % ethane, and small quantities of saturated C_3 - to C_6 -hydrocarbons. The gaseous products contained all the carbon originally present in the carbide. Hydrolysis, at 80°, of monocarbide specimens containing dispersed uranium metal yielded the expected gaseous products and an additional 2 moles of hydrogen per mole of uranium metal. The rate of hydrolysis was studied briefly.

Introduction

Since the hydrolysis of uranium carbides in aqueous systems has received little attention in earlier work, a program was initiated in this Laboratory to study the process. The results of

the first phase of this program, on the hydrolysis of uranium monocarbide between 25 and 99°, are given in this paper. Previously, Litz² studied this reaction; however, he worked only at temperatures above 83° and did not measure

(1) Operated by Union Carbide Nuclear Co. for the U. S. Atomic Energy Commission.

(2) L. M. Litz, "Uranium Carbides; Their Preparation, Structure, and Hydrolysis," Ph.D. Thesis, Ohio State University, 1945.