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The Kinetics of Pyridine-Catalyzed Hydrolysis of Chloropentaphenylcyclotriphosphonitrile[1]

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For the pyridine-catalyzed hydrolysis of chloropentaphenylcyclotriphosphonitrile in acetone, over 90% of the reaction occurs according to the equation

$$(C_6H_5)_5ClP_3N_3 + H_2O + C_5H_5N = (C_6H_5)_5(OH)P_3N_3 + C_5H_5NHCl$$

Kinetic data support a nucleophilic base-catalysis mechanism

$$(C_6H_5)_5ClP_3N_3 + C_5H_5N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_5P_3N_3 \cdot C_5H_5N^+ + Cl^-$$

$$(C_6H_5)_5P_3N_3 \cdot C_5H_5N^+ + H_2O \xrightarrow{k_3} (C_6H_5)_5(OH)P_3N_3 + C_5H_5NH^+$$

Computer analysis of the data gave an average value of $k_1 = (1.2 \pm 0.1) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ at 25° in a solution containing 0.100 M pyridinium tetrafluoroborate. The new compounds fluoropentaphenylcyclotriphosphonitrile and N-pentaphenylcyclotriphosphonitrilopyridinium perchlorate were isolated.

Introduction

Despite favorable thermodynamic stability of halophosphonitrile polymers, the sensitivity of these compounds to hydrolysis has greatly restricted their utilization. Whereas considerable research has been devoted to the synthesis of phosphonitriles which are both thermally stable and chemically inert,[3,4] few kinetic studies of nucleophilic substitution on halophosphonitriles[5-11] and none of the hydrolysis of small-ring halophosphonitriles have been undertaken.

A kinetic study was undertaken of pyridine-catalyzed hydrolysis of chloropentaphenylcyclotriphosphonitrile. This phosphonitrile was selected as the substrate because it contained only one reaction site and one replaceable chlorine, a feature which was expected to simplify interpretation of the kinetic data. Information on this model system was expected to provide insight into the more general subject of base-catalyzed nucleophilic substitution of phosphonitriles. One of the rewards of a kinetic study is the assistance it provides in preparing new compounds from a knowledge of mechanisms. In the present study it was possible to prepare the new compounds fluoropentaphenylcyclotriphosphonitrile and N-pentaphenylcyclotriphosphonitrilopyridinium perchlorate by applying simple mechanistic reasoning.

(1) Abstracted in part from the Ph.D. thesis of V. R. Miller, Southern Illinois University, 1968.
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Results and Discussion

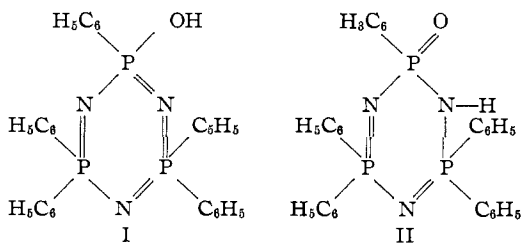
It had been shown previously that $(C_6H_5)_5ClP_3N_3$ and water react in pyridine to give approximately a 95% yield of $(C_6H_5)_5(OH)P_3N_3$.[12] In acetone, the solvent used for the kinetic studies, a similar observation was made for the pyridine-catalyzed hydrolysis. It was possible to account for 96% of the reactant chloropentaphenyltriphosphonitrile in the form of the products $(C_6H_5)_5(OH)P_3N_3$ and $[(C_6H_5)_5P_3N_3]_2O$. Of this amount approximately 91% of the chloropentaphenyltriphosphonitrile is consumed according to eq 1.

$$(C_6H_5)_5ClP_3N_3 + H_2O + C_5H_5N \xrightarrow{\text{acetone}} (C_6H_5)_5(OH)P_3N_3 + C_5H_5NHCl \quad (1)$$

The remaining 9% of the $(C_6H_5)_5ClP_3N_3$ is used up in a side reaction which produces $[(C_6H_5)_5P_3N_3]_2O$.[12]

$$(C_6H_5)_5ClP_3N_3 + (C_6H_5)_5(OH)P_3N_3 + C_5H_5N \xrightarrow{\text{acetone}} [(C_6H_5)_5P_3N_3]_2O + C_5H_5NHCl \quad (2)$$

This minor side reaction was ignored in the treatment of kinetic data. Although the structure of $(C_6H_5)_5(OH)P_3N_3$ is not known with certainty, there is strong evidence in favor of structure I.[12] Any rearrangement which might occur between structures I and II is considered rapid, would occur after the rate-controlling step, and, therefore, would not be kinetically measurable.



I

II

It was not possible to fit the kinetic data to any

(12) C. D. Schmulbach and V. R. Miller, *Inorg. Chem.*, **5**, 1621 (1966).

simple rate law, even when the concentrations of water and pyridine were much higher than the concentration of $(C_6H_5)_5ClP_3N_3$. Experiments showed that the product pyridinium chloride retarded the reaction. Additional experiments were undertaken to determine whether the species responsible for the retardation was the pyridinium ion or the chloride ion. The results of these experiments are shown in Figure 1. The concentrations of $(C_6H_5)_5ClP_3N_3$ (1.00×10^{-2} M), water (0.553 M), and pyridine (0.621 M) were the same for all runs. A quantity of the appropriate salt was added to the individual runs to give nearly equal initial concentrations—1.00×10^{-4} M tetraethylammonium chloride, 0.99×10^{-4} M pyridinium chloride, and 1.00×10^{-4} M pyridinium tetrafluoroborate. No extra salt was added to the sample used for the control experiment.

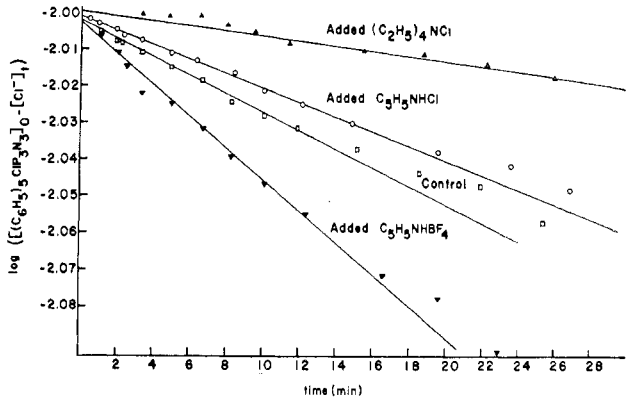


Figure 1.—Effect of added salts on the rate of hydrolysis of $(C_6H_5)_5ClP_3N_3$.

It is obvious from these data that the chloride ion and not the pyridinium ion retards the rate of the reaction. Also, the pyridinium chloride is less effective than the tetraethylammonium chloride in retarding the reaction. This difference in behavior can be accounted for only in terms of extensive ion pairing in the pyridinium chloride system. Experiment confirmed this conclusion. Conductance measurements of 9.9×10^{-4} M pyridinium chloride, tetraethylammoniun chloride, and pyridinium chloride in 0.621 M pyridine–0.55 M H_2O–acetone gave molar conductances of 25, 153, and 157 ohm^{-1} cm^{-1} mol^{-1}, respectively. The value of the pyridinium chloride ion association constant, K_A, is 270 M^{-1} when measured in 0.621 M pyridine–1.107 M H_2O–acetone. This value is highly dependent upon the concentration of water. The rate-accelerating effect of pyridinium tetrafluoroborate is readily understood in terms of this equilibrium. The addition of pyridinium ions increases the concentration of the pyridinium chloride ion pairs while reducing the concentration of the rate-retarding chloride ions.

All mechanisms which do not include the formation of chloride in a reversible step can be ruled out. The choice of reasonable mechanisms is reduced to two. The first involves nucleophilic catalysis by pyridine (eq 3 and 4). On the basis of the steady-state approximation, the rate law derived for this mechanism is given in eq 5.

$$(C_6H_5)_5ClP_3N_3 + C_5H_5N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_5P_3N_3\cdot C_5H_5N^+ + Cl^- \quad (3)$$

$$(C_6H_5)_5P_3N_3\cdot C_5H_5N^+ + H_2O \xrightarrow{k_3} (C_6H_5)_5(OH)P_3N_3 + C_5H_5NH^+ \quad (4)$$

$$\text{rate} = \frac{k_1[(C_6H_5)_5ClP_3N_3][C_5H_5N][H_2O]}{(k_2/k_3)[Cl^-] + [H_2O]} \quad (5)$$

Another reasonable mechanism involves ionization of $(C_6H_5)_5ClP_3N_3$, possibly solvent assisted, followed by a general base-catalyzed attack by water (eq 6 and 7). The rate law for this mechanism which assumes a steady-state approximation is shown in eq 8.

$$(C_6H_5)_5ClP_3N_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_5P_3N_3^+ + Cl^- \quad (6)$$

$$(C_6H_5)_5P_3N_3^+ + C_5H_5N\cdot H_2O \xrightarrow{k_3} (C_6H_5)_5(OH)P_3N_3 + C_5H_5NH^+ \quad (7)$$

$$\text{rate} = \frac{k_1[(C_6H_5)_5ClP_3N_3][C_5H_5N\cdot H_2O]}{(k_2/k_3)[Cl^-] + [C_5H_5N\cdot H_2O]} \quad (8)$$

The nucleophilic catalysis mechanism (eq 3 and 4) was established more firmly by experiments in which high pyridinium ion concentrations were used to reduce the $(k_2/k_3)[Cl^-]$ term in the denominator of eq 5 to insignificance compared to the concentration of water. The pseudo-first-order plots of the data from these experiments are independent of the water concentration and dependent upon the pyridine concentration. Such a behavior would be anticipated for a rate law defined by eq 5. At the same time the general base catalyzed mechanism (eq 6 and 7) is eliminated since the rate would be independent both of the water and the pyridine concentration. The values of k_1 obtained graphically from the linear portions of the plots (up to 20% reaction) are recorded in Table I. They are in fair agreements with the values of k_1 obtained by computer analysis of the data.

Arguments against the general base catalysis mechanism were also obtained from qualitative competition experiments When $(C_6H_5)_5ClP_3N_3$, NH_4F, water, and pyridine were allowed to react in acetone, both $(C_6H_5)FP_3N_3$ and $[(C_6H_5)_5N_3]_2O$ were isolated. For the same mixture without pyridine, only unreacted $(C_6H_5)_5ClP_3N_3$ was isolated. It is possible to account for the pyridine catalysis of the reaction of $(C_6H_5)_5ClP_3N_3$ with H_2O by proposing a complex between pyridine and H_2O (general base catalysis) or by nucleophilic catalysis as described in eq 3 and 4. However, it is not possible to propose general base catalysis for fluoridation. If the assumption is made that both fluoridation and hydrolysis occur by the same mechanism, the only way that pyridine can catalyze the reaction is to form a complex with the $(C_6H_5)_5ClP_3N_3$.

The synthesis of $[(C_6H_5)_5P_3N_3(C_5H_5N)^+][ClO_4^-]$ showed that the pyridiniumphosphonitrile cation is a stable species. This provides additional support for the nucleophilic catalysis mechanism, which includes

TABLE I

SPECIFIC RATE CONSTANTS OBTAINED FROM COMPUTER ANALYSIS AND PSEUDO-FIRST-ORDER PLOTS

	Graphic		Computer				
Run no.[a]	$[C_5H_5N]$, M	$[H_2O]$, M	$10^{-3}k_1$,[b] M^{-1} sec^{-1}	$10^{-3}k_1$,[b] M^{-1} sec^{-1}	k_2, M^{-1} sec^{-1}	$10^{-3}k_3$,[c] M^{-1} sec^{-1}	$10^{-3}\Phi$,[d] M^2
13[e]	0.621	1.107	...	2.71	0.35	0.2	1.1
6[f]	0.497	0.221	1.04	1.21	0.50	5.4	52.6
7[f]	0.497	0.443	1.16	1.25	0.21	1.9	18.0
8[f]	0.497	1.328	1.10	1.15	0.10	1.1	7.5
9[f]	1.241	0.221	0.97	1.16	0.30	1.9	8.2
10[f]	1.241	0.443	0.93	1.05	0.17	0.9	5.5
11[f]	1.241	1.328	0.95	1.09	3.62	7.6	25.6

[a] The concentration of chloropentaphenyltriphosphonitrile is 1.00×10^{-2} M for all runs. [b] The values of k_1 are obtained by dividing the observed k_1 by the concentration of pyridine. [c] The values of k_3 are obtained by dividing the observed k_3 by the concentration of water. [d] $\Phi = \Sigma([Cl^-]_{exptl} - [Cl^-]_{calcd})^2$. [e] Pyridium chloride association constant, $K_A = 270$ M^{-1}, was used in this computation. [f] Sample also contains 0.100 M pyridinium tetrafluoroborate.

the $(C_6H_5)_5P_3N_3(C_5H_5N)^+$ ion as a reaction intermediate. Furthermore, the concept of nucleophilic catalysis by pyridine and imidazole of hydrolysis or solvolysis of phosphates is well documented.[13] A computer method developed by Ball and Groenweghe[14] for the analysis of complicated rate data was modified to evaluate the rate constants for the nucleophilic catalysis mechanism (eq 3 and 4). This method requires the solution of simultaneous differential equations. It is unnecessary to make the steady-state assumption in this analysis. The basic concepts which are utilized in the computer analysis are simple. The two differential equations are written into the program. Estimates of the rate constants (k_1, k_2, and k_3) and the experimental times and corresponding chloride concentrations for a single kinetic experiment are introduced into the computer. The computer calculates a theoretical concentration of chloride for each experimental time by solving the simultaneous differential equations to which arbitrary values of the specific rate constants have been assigned. The calculated chloride concentrations are then compared to the experimental values. By an iterative technique the computer adjusts the specific rate constants to minimize the difference between the experimental and the calculated concentrations. The fit between experimental and calculated chloride concentrations is reflected in the value of Φ, where $\Phi = \Sigma([Cl^-]_{exptl} - [Cl^-]_{calcd})^2$. A small value of Φ indicates that the choice of the mechanism as reflected in the differential equations is reasonable. A test of the sensitivity of the program to changes in the rate constants showed a greater sensitivity of Φ to the values of k_1 than to those of k_2 and k_3. Because of the lower sensitivity of the computer analysis to k_2 and k_3, these values are considered to be good only to within an order of magnitude.

To this point several factors have been ignored in developing the mechanism of hydrolysis of $(C_6H_5)_5ClP_3N_3$. Elimination of these factors in the treatment of the data does not affect the basic conclusion that the major path for reaction is nucleophilic catalysis by pyridine. Recognition emphasizes the great complexity of this system. It was observed that hydrolysis proceeds in the absence of pyridine at a very slow but measurable rate. The solvent may or may not be participating in this minor uncatalyzed path. In any case, the contribution of this mechanism to the overall rate was considered immeasurably small.

The hydrolysis of pyridine to give the pyridinium ion and hydroxide ion is a possibility. This equilibrium cannot be involved in the major path of hydrolysis. If it were, the hydrolysis reaction would be retarded by pyridinium ion. This is not the case. Although an equilibrium between water and pyridine and a 1:1 pyridine–water[15] complex is reasonable, even expected, no kinetic evidence for it was found.

Experimental Section

Reagents.—Reagent grade pyridine (Fisher or Mallinckrodt) was purified by two fractional distillations from potassium hydroxide. The pyridine was stored over molecular sieves (Linde 4A) before use to remove the last trace of water. Reagent grade acetone (Baker and Adamson or Matheson Coleman and Bell) was purified by fractional distillation and stored for at least 24 hr over molecular sieves before use. The acetone was used within 1 week after being dried over molecular sieves.

Pyridinium chloride was prepared by passing hydrogen chloride gas into a solution of 10 ml of pyridine in 100 ml of benzene and filtering the pyridinium chloride in the absence of air. It was purified by vacuum sublimation to give colorless crystals; mp 146.5–147.0°, lit.[16] mp 146.0°.

Pyridinium tetrafluoroborate was prepared by slowly adding 25.0 ml, a slight excess, of pyridine to 54 g of 48% aqueous tetrafluoroboric acid (Matheson Coleman and Bell) in 100 ml of water, evaporating to near dryness, and filtering. The impure salt was recrystallized from ethanol–pyridine solution and dried at 2 mm and room temperature to give colorless crystals; mp 220–222°, lit.[17] mp 217°.

The preparation of $(C_6H_5)_5ClP_3N_3$ has been described previously.[12]

$(C_6H_5)_5P_3N_3 \cdot (C_5H_5N)ClO_4$.—All manipulations were done on a vacuum line, except the handling of the solid product. The latter could be done in a dry bag.

A sample of 0.174 g (8.4×10^{-4} mol) of anhydrous $AgClO_4$ (G. Fredrick Smith) and 0.484 g (8.7×10^{-4} mol) of $(C_6H_5)_5ClP_3N_3$ were placed in a 100-ml flask. About 0.2 ml of pyridine along with 20 ml of acetonitrile was transferred to the flask. The reaction was allowed to proceed for 3 hr at room temperature with intermittent stirring. A 0.1-g sample (20% theoretical) of analytically pure $(C_6H_5)_5P_3N_3(C_5H_5N)ClO_4$, mp 196–197° dec, was recovered.

Anal. Calcd for $C_{35}H_{30}ClN_4O_4P_3$: C, 60.14; H, 4.33; Cl, 5.07; N, 8.02; P, 13.29. Found: C, 60.87; H, 4.29; Cl, 4.62; N, 8.09; P, 12.77.

Infrared spectral bands for this compound are summarized in Table II.

Hydrolysis of this compound in acetonitrile gave $[(C_6H_5)_5P_3N_3]_2O$ and pyridinium perchlorate.

Stoichiometry.—To establish the stoichiometry of the hydrolysis reaction, 1.014 g (1.82 mmol) of $(C_6H_5)_5ClP_3N_3$ was dissolved in 25 ml of acetone which also contained 1.24 M pyridine,

(13) See, for example, P. S. Traylor and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 553 (1965); W. P. Jencks and M. Gilchrist, *ibid.*, **87**, 3199 (1965); R. Blakeley, F. Kerst, and F. H. Westheimer, *ibid.*, **88**, 112 (1966).

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TABLE II

INFRARED SPECTRA (CM^{-1}) OF PHOSPHONITRILES[a]

Assignment	RCl	RF	ROH	ROR	$R \cdot C_5H_5N^+ \cdot ClO_4^-$
C—H	3054 vw	3050 vw	3050 vw	3050 vw	3056 vw
O—H			2640 vw		
Pyridine					1614 w
Phenyl	1588 vw	1590 vw	1588 vw	1588 vw	1588 vw
Phenyl	1479 w	1480 w	1480 w	1480 w	1480 w
		1446 w			
Phenyl	1437 m	1437 s	1438 m	1437 m	1437 m
			1365 m		
P=N—P	1204 vs	1202 vs	1230 vs	1195 vs	1209 vs
	1193 sh		1202 vs		1189 vs
	1167 vs	1174 vs	1176 s	1171 vs	1169 vs
	1156 sh		1150 s		
P—C	1120 m	1122 m	1121 s	1120 m	1119 m
ClO_4^-					1088 s
Phenyl	1067 w	1068 vw	1066 vw	1066 vw	1065 sh
Phenyl	1026 w	1028 m	1026 w	1025 w	1024 w
Pyridine					1013 w
Phenyl	996 w	998 w	995 w	996 v	997 w
					935 w, b
P—O			952 s	946 m	
		876 m			
	853w	870 m	844 m	851 w	850 w
		812 m	827 w	809 w	
		768 m		767 w	
		760 sh	762 w		
	746 m	747 m	742 m	742 m	748 m
Phenyl	725 s	724 s	723 s	720 s	724 s
	721 sh				
	713 w	708 m		708 m	
Phenyl	695 s	696 s	692 s	692 s	693 s
Pyridine					677 sh
Pyridine					622 m
			601 m		
	553 vs	544 vs	545 vs	550 vs	550 vs
	523 s	517 sh			
	512 m	511 s	512 vs	512 s	515 s
P—Cl	499 w				
	437 m	432w	422 w	428 w	425 w

[a] R = $(C_6H_5)_5P_3N_3$.

0.100 *M* pyridinium tetrafluoroborate, and 2.43 *M* water. After 21 hr at 25° the solvent was removed at a reduced pressure and the residual oil was shaken with acetonitrile. It was possible to isolate 0.773 g (1.44 mmol) of $(C_6H_5)_5(OH)P_3N_3$ (mp 269–271°). A sample of 0.163 g (0.15 mmol) of $[(C_6H_5)_5P_3N_3]_2O$ was also isolated. This constitutes 96% accountability for the P–N products of this reaction.

Kinetic Procedure.—Electrical potentials were measured with a Beckman Research pH meter. The reference electrode was a saturated calomel electrode. A saturated potassium nitrate bridge as described by Matsuyama[18] was used.

The working electrode was a strip of silver foil 5.0 mm wide, coated with silver chloride by a modification of a method described by Ives and Janz.[19] The holder was designed so that the solution was protected from air currents.

The appropriate weight of finely ground $(C_6H_5)_5ClP_3N_3$ was placed in a 25-ml flask and the acetone containing the appropriate amounts of the other components was placed in a second flask. Both flasks and their contents were thermally equilibrated at 25.0 ± 0.1° for at least 15 min. To start the reaction the solvent was transferred to the flask containing the phosphonitrile which was then shaken to effect solution. The time for dissolution was less than 0.2 min. At the appropriate intervals 1.00-ml aliquots were withdrawn and delivered, with stirring, into 10.00 ml of quenching solution. The concentration of H_2SO_4 in this solution was chosen so that approximately 5×10^{-3} *M* H_2SO_4 remained after the pyridine was neutralized. Although a precipitate was formed, it did not affect the measurements. The solution was placed in the constant-temperature bath for 10–15 min and then was placed in contact with the electrodes for another 2 min before the potential was measured. The electrodes were not rinsed between solutions. It was found that rinsing them made it necessary to use longer equilibration times. The concentrations of chloride ion were obtained from a calibration curve.

The concentration of H_2SO_4 in the quenching solution was found to be important. For 0.9 *M* H_2SO_4 there is a time-dependent change in the potential that corresponded to an increase in the chloride ion concentration. Presumably this is due to a slow acid-catalyzed hydrolysis of $(C_6H_5)_5ClP_3N_3$. At 0.067 *M* H_2SO_4 this time-dependent change was not observed. Experiments showed that $(C_6H_5)_5(OH)P_3N_3$ and $(C_6H_5)_5ClP_3N_3$ had no effect on the potential.

Since the concentration of pyridine in the reaction solution has an effect on the potential developed, a calibration curve for each series of runs at given pyridine concentrations was prepared. The accuracy of the determination of the concentration of chloride was estimated to be better than ±3% in the range 10^{-2}–10^{-3} *M* and better than ±10% below 10^{-3} *M*.

In two different experiments $(C_6H_5)_5ClP_3N_3$ was allowed to react either with NaF or NH_4F. In both cases $(C_6H_5)_5FP_3N_3$ was isolated. In one experiment 0.28 g (0.50 mmol) of $(C_6H_5)_5ClP_3N_3$, 0.80 g (22 mmol) of NH_4F, and 10.0 ml of pyridine were diluted to 50.0 ml with acetone which contained a small amount of water. Not all the NH_4F dissolved. After 24 hr at 25° the reddish solution was evaporated to dryness, shaken with 50 ml of acetonitrile, and the unreacted NH_4F was removed by filtration. The solution was again evaporated to dryness, shaken with 20 ml of CH_3CN, and filtered to give a fraction melting at 153–154°. This process was repeated until 0.14 g (52% yield) of $(C_6H_5)_5FP_3N_3$ was obtained. The filtrate contained a difficultly separable mixture of phosphonitriles. No $(C_6H_5)_5ClP_3N_3$ was isolated. Infrared spectroscopy was used to identify $[(C_6H_5)_5P_3N_3]_2O$ in the residue. The impure $(C_6H_5)_5FP_3N_3$ was recrystallized from CH_3CN to give an analytically pure sample, mp 154–154.5°.

Anal. Calcd for $C_{30}H_{25}FN_3P_3$: C, 66.79; H, 4.67; F, 3.52; N, 7.77; P, 17.22. Found: C, 67.15; H, 4.76; F, 3.23; N, 7.82; P, 17.23.

The infrared spectral bands are given in Table II.

To prove that fluoridation is pyridine catalyzed, a reaction similar to that just described was carried out in the absence of pyridine. A sample of 0.32 g (0.57 mmol) of $(C_6H_5)_5ClP_3N_3$ and 0.82 g (22 mmol) of NH_4F was diluted to 50 ml with acetone. In this case after 25 hr at 25° a clear solution was obtained and 0.16 g (0.26 mmol) or 48% of unreacted $(C_6H_5)_5ClP_3N_3$, mp 148–150°, was recovered. No characterizable compounds could be isolated from the viscous oil that remained.

Two quantitative experiments were performed to show the influence of water on the ion-pair association constant of pyridinium chloride. The conductance of various concentrations of pyridinium chloride in 1.107*M* H_2O or 0.553 *M* H_2O and 0.621 *M* pyridine in acetone was analyzed by means of a computer program developed by Kay.[20] A value of 270 M^{-1} for K_A was obtained for the solution containing 1.107 *M* H_2O. Although no value could be obtained for the 0.553 *M* H_2O solution the data showed that it would be greater than the 270 M^{-1} calculated for the 1.107 *M* H_2O solution.

Infrared spectra were taken on a Beckman IR10 spectrophotometer as Nujol and hexachlorobutadiene mulls. Plates of potassium bromide or cesium bromide were used as windows.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were taken in open capillaries and are uncorrected.

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