

53. *Hydrolysis of Dialkylphosphinic Fluorides and Dialkyl Phosphorofluoridates. Kinetic and Tracer Studies.*

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During hydrolysis in H_2^{18}O , no appreciable oxygen exchange occurs between water and the phosphoryl group of dimethylphosphinic fluoride, diethylphosphinic chloride, or diisopropyl phosphorofluoridate. A method for determining ^{18}O in >PO-OH groups is described. The uncatalysed hydrolysis of dimethylphosphinic fluoride is compared with that of some other acid halides. The deuterium isotope effect on the rate of the uncatalysed and of the acid-catalysed hydrolysis of diisopropyl phosphorofluoridate has been measured. Dimethylphosphinic fluoride has been synthesised from dimethylphosphinic chloride and sodium fluoride. Its hydrolysis is acid- and base-catalysed. The rate-determining step in the hydrolysis of these fluorides seems to involve both proton-transfer and nucleophilic attack.

THE solvolysis of phosphinic chlorides and phosphorochloridates has been shown to involve bimolecular nucleophilic displacement ($\text{S}_{\text{N}}2$) and not rapid reversible formation of unstable intermediates of quinquevalent phosphorus.¹ Hydrolysis of these phosphorus chlorides is base-catalysed, but is unaffected by acids. In contrast, hydrolysis of dialkyl phosphorofluoridates is also acid-catalysed.^{2,3} Similarly, the solvolysis of various alkyl and substituted benzyl fluorides is acid-catalysed, while there is no such catalysis in the reactions of the corresponding chlorides.⁴

Search for Intermediates: ^{18}O -Exchange Studies.—Oxygen-exchange during hydrolysis of various carbonyl compounds has been observed;⁵ and exchange of oxygen in solutions of several inorganic phosphorus acids has been measured.⁵ On the other hand, no oxygen-exchange was observed during the uncatalysed hydrolysis of phenyl phosphate.⁶ Similarly, in the hydrolysis of several monoalkyl or aryl phosphates catalysed by prostatic acid phosphatase there was no evidence for reversible formation of an intermediate with five groups bonded to phosphorus.⁷

An expansion of the valency shell of phosphorus by interactions of *d*-orbitals and formation of unstable quinquevalent intermediates is however *a priori* possible in reactions at phosphorus atoms. As an example of a stable quinquevalent compound of phosphorus, the successful preparation of pentaphenylphosphorus⁸ may be cited.

The hydrolysis of diisopropyl phosphorofluoridate is subject to general acid- and base-catalysis.³ Various mechanisms were proposed which all involved reversible addition of water to the phosphoryl group as a preliminary step.³

In the present work, evidence was sought for formation of intermediates during hydrolysis of phosphoryl compounds having substituents of different electronegative properties. No such evidence was found in the hydrolysis of diethyl phosphorochloridate.¹ A change in the direction which was thought to favour formation of intermediates was substitution of fluorine for chlorine. Fluorine is more electronegative than chlorine,⁹ and the phosphorus-fluorine bond is stronger. It seemed therefore more likely that fast reversible addition of water to the phosphoryl group should be followed by a rate-determining

¹ Dostrovsky and Halmann, *J.*, 1953, 502, 516; 1956, 1004.

² Waters and de Worms, *J.*, 1949, 926.

³ Kilpatrick and Kilpatrick, *J. Phys. Colloid Chem.*, 1949, **53**, 1371, 1385.

⁴ Miller and Bernstein, *J. Amer. Chem. Soc.*, 1948, **70**, 3600; Chapman and Levy, *J.*, 1952, 1673.

⁵ Bender, Ginger, and Unik, *J. Amer. Chem. Soc.*, 1958, **80**, 1044, giving previous references; Brodskii and Sulima, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 589.

⁶ Stein and Koshland, *Arch. Biochem. Biophys.*, 1952, **39**, 229.

⁷ Bunton, Silver, and Vernon, *Proc. Chem. Soc.*, 1957, 348.

⁸ Wittig and Riber, *Annalen*, 1949, **562**, 187.

⁹ Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1940, p. 60.

ing dissociation of fluorine than of chlorine from phosphorus. The hydrolysis of dimethylphosphinic fluoride and of diisopropyl phosphorofluoridate was carried out in ^{18}O -enriched water, and the phosphoryl group was analysed for ^{18}O content.

Dimethylphosphinyl fluoride was prepared by reaction of dimethylphosphinic chloride with sodium fluoride: $\text{Me}_2\text{POCl} + \text{NaF} = \text{Me}_2\text{POF} + \text{NaCl}$. The synthesis of several other dialkylphosphinic fluorides has recently been reported.¹⁰

Results for the hydrolysis of several phosphorus halides are given in Table 1. In experiments (a) and (c) the phosphorus halides were hydrolysed for more than ten half-times. The resulting dialkylphosphinic acid was analysed for ^{18}O -enrichment in the

TABLE 1. Hydrolysis of phosphorus halides in ^{18}O -enriched water at 25° .

Phosphorus halide	Milli-moles	Water		Reaction (%)	Atom % ^{18}O excess in $\text{PO}\cdot\text{OH}$	
		Milli-moles	Atom % ^{18}O Excess		Found	Calc. for no exchange
(a) Me_2POF	1.40	16.5	1.17	100	0.60	0.59
(b) Me_2POF	1.30	556	1.17	50	0.02	0
(c) Et_2POCl	0.65	9.0	7.69	100	3.66	3.85
(d) $(\text{Pr}^i\text{O})_2\text{POF}$...	0.406	278	2.26	30	0.02	0
(e) $(\text{Pr}^i\text{O})_2\text{POF}$...	0.33	280*	2.08	47	0.005	0

* Containing 0.093 millimole of HCl per l.

$\text{PO}\cdot\text{OH}$ group by the carbodi-imide method (see p. 309). In the other cases the unchanged phosphorus halide was extracted after partial hydrolysis, by chloroform for dimethylphosphinyl fluoride and by *n*-hexane for diisopropyl phosphorofluoridate.

In every case the observed value was close to that calculated for hydrolysis without exchange. Similar conclusions have been reached for the base-catalysed hydrolysis of phosphorus fluorides.¹¹

Uncatalysed Hydrolysis of Phosphorus Fluorides.—For a discussion of the difference in reactivity of dialkyl phosphoro-chloridates and -fluoridates, the rate of the uncatalysed ("water") reaction of the phosphorus fluorides will be compared with the rate of hydrolysis of similar chlorides.

The rate of hydrolysis of diisopropyl phosphorofluoridate in ordinary water has been measured by several methods.^{2,3} The kinetics in ordinary water are complicated by autocatalysis by the product, diisopropyl hydrogen phosphate. At constant pH, the hydrolysis obeys first-order kinetics. Kilpatrick and Kilpatrick³ measured the hydrolysis in buffer solution and determined the catalytic coefficients of the various components. By elimination of the parts of the reaction due to the catalysts, the rate constant of the water reaction, k_w , was found³ to be $72 \times 10^{-4} \text{ hr.}^{-1}$ at 25° . Waters and de Worms² measured the hydrolysis in ordinary water, and from the initial rate estimated k_w to be $60 \times 10^{-4} \text{ hr.}^{-1}$ at 25° .

It seemed of interest to find a method of measuring the rate of the uncatalysed hydrolysis directly, by using a buffer system which contributes as little as possible to the reaction. The system fluoride ion-hydrofluoric acid, proposed by Bell and McCoubrey,¹² was very effective in decreasing the extent of the catalysed reactions in the hydrolysis of diisopropyl phosphorofluoridate. The relatively low dissociation constant of hydrofluoric acid¹³ ($K_A = 6.7 \times 10^{-4}$) ensures a low hydrogen-ion concentration, while the nucleophilic activity of the fluoride ion has no influence since the starting material is regenerated with the phosphorofluoridate.

In the present work, diisopropyl phosphorofluoridate was hydrolysed in aqueous sodium fluoride; the buffering action was sufficient to keep the concentration of hydrogen ions very low. The reaction followed first-order kinetics, which proved that the catalytic

¹⁰ Dawson and Kennard, *J. Org. Chem.*, 1957, **22**, 1671.

¹¹ Larsson, *Acta Chem. Scand.*, 1957, **11**, 1139.

¹² Bell and McCoubrey, *Proc. Roy. Soc.*, 1956, **234**, A, 192.

¹³ McCoubrey, *Trans. Faraday Soc.*, 1955, **51**, 743.

effect of undissociated hydrofluoric acid is negligible. At 25°, $k_1 = 62 \times 10^{-4}$ hr.⁻¹, in good agreement with published results.^{2, 3}

The hydrolysis of dimethylphosphinic fluoride in ordinary water obeyed first-order kinetics, and the rate was similar to that measured in sodium fluoride solution. At 25°, $k_1 = (4 \pm 1) \times 10^{-4}$ sec.⁻¹. Its half-time is thus 1/230 that of diisopropyl phosphorofluoridate. The absence of autocatalysis in this case can be explained by the small dissociation constant of the product, dimethylphosphinic acid, the p*K* of which is about 3.1. The hydrogen-ion concentration from this acid and from hydrogen fluoride is insufficient to cause appreciable acid-catalysis. In 0.01*N*-hydrochloric acid, and in 0.05*N*-sodium hydroxide hydrolysis was complete within a few minutes.

In Table 2, the rates of hydrolysis of diisopropyl phosphorofluoridate at several temperatures are listed. From the temperature-dependence of the rate of hydrolysis, parameters of the Arrhenius equation were calculated: $k_1 = 0.88 \times 10^{10} \exp(-21,800/RT)$ sec.⁻¹.

TABLE 2. *Hydrolysis of diisopropyl phosphorofluoridate in sodium fluoride solutions.*

Temp.	24.85°	24.85°	30.40°	30.40°	40.08°	40.08°
POF(OPr ⁱ) ₂ (millimole)...	0.62	0.20	0.62	0.20	0.20	0.76
NaF (millimole)	24.5	24.5	24.5	24.5	24.5	6.1
10 ³ <i>k</i> ₁ (hr. ⁻¹)	6.2	6.2	12.4	11.8	37.8	36.4

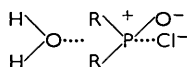
In the acid-catalysed hydrolysis of diisopropyl phosphorofluoridate, a much lower activation energy of 13.5 kcal. mole⁻¹ has been observed.³ Acid-catalysis is therefore due to reduction in the activation energy. The assumption³ that the temperature coefficients of the uncatalysed and of the acid-catalysed hydrolysis are equal is thus untenable.

Comparison of Rates of Hydrolysis of Acid Fluorides and Chlorides.—In the previous section, the activation energy for the uncatalysed hydrolysis of diisopropyl phosphorofluoridate was reported as 21.8 kcal./mole. For the hydrolysis of diisopropyl phosphorochloridate, the much lower value of 14.4 has been reported.¹ Results for some other fluoro- and chloro-compounds are compared in Table 3. For the few compounds on which

TABLE 3. *Hydrolysis of fluorides and chlorides of phosphorus, sulphur, and carbon, at 25°.*

Acid halide	Solvent	10 ³ <i>k</i> ₁ (sec. ⁻¹)	Δ <i>E</i> * (kcal. mole ⁻¹)	Δ <i>S</i> * (cal. deg. ⁻¹)	<i>k</i> _{RCI} / <i>k</i> _{RF}	Ref.
Me ₂ POF	H ₂ O	4	—	—	—	
Me ₂ POCl	EtOH (−8.5°)	60	—	—	—	1
(Pr ⁱ O) ₂ POF	H ₂ O	0.017	21.8	−12.7	} 5000	1
(Pr ⁱ O) ₂ POCl	H ₂ O	81	14.4	−20.6		
Ph·SO ₂ F	50% COMe ₂	<5 × 10 ⁻⁴	—	—	} <5000	14
Ph·SO ₂ Cl	"	2.4	14	−29		
Me·COF	75% COMe ₂	1.1	—	—	} 8000	14
Me·COCl	"	8600	14	−14		
Ph ₃ CF	85% COMe ₂	0.027	22.6	−10	} 1 × 10 ⁶	14
Ph ₃ CCl	"	27,000	12.5	−17		

measurements at several temperatures have been made, the lower rate of hydrolysis of the fluoro-compound is due to a higher activation energy, and is in spite of a less negative entropy of activation. The ratio of the rates for chloro- and fluoro-compounds (Table 3) is similar for halides of phosphorus, sulphur, and carbon. The larger activation energy in fluoro-compounds seems to be connected with the larger bond energy of fluorine.⁸ The more negative entropy of activation of acid chlorides seems due to the highly ordered, and possibly strained, transition state, *e.g.*,



The Deuterium Isotope Effect in Hydrolysis.—Comparison of the rates of solvolysis of various compounds in normal water and in deuterium oxide has sometimes been of use in

¹⁴ Swain and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 246.

deciding between specific acid-catalysed reactions involving a fast reversible proton-addition followed by slow formation of the products, and proton-transfer in the rate-determining step.¹⁵ The rate of hydrolysis of diisopropyl phosphorochloridate in deuterium oxide has been found¹ to be slightly smaller than that of water ($k_D/k_H = 0.8$).

In the present work the rate of solvolysis of diisopropyl phosphorofluoridate was

TABLE 4. Deuterium isotope effect in the solvolysis of diisopropyl phosphorofluoridate.

Temp.	POF(OPr ⁱ) ₂ (millimole) initially)	Solvent	Acid or buffer (millimole)	10 ⁴ k ₁ (min. ⁻¹)	k _D /k _H
24.85°	16.8	H ₂ O	HCl 48.8	32.5 ± 1.0	0.94 ± 0.03
"	12.3	99.2% D ₂ O	DCl 52.0	32.4 ± 1.2	
"	15.7	95% D ₂ O	DCl 46.4	27.8 ± 2.2	
"	15.5	H ₂ O	HCl 20.7	16.7 ± 1.2	
"	14.8	95% D ₂ O	DCl 22.5	17.6 ± 2.9	0.87 ± 0.06
40.08°	0.76	H ₂ O	NaF 6.09	6.3 ± 0.5	
"	0.71	95% D ₂ O	NaF 4.53	5.5 ± 0.4	

measured in water and in deuterium oxide. The rates in water compared well with those reported by Waters and de Worms.² Table 4 lists first-order rate constants and their probable errors. The last two runs noted show the deuterium isotope effect in the uncatalysed hydrolysis in a sodium fluoride buffer.

In most acid-catalysed reactions the rate of solvolysis is larger in D₂O than in water. In these reactions a prior fast equilibrium between the acid and the substrate to form a protonated substrate is assumed to be followed by slow decomposition to the products. Most of the above reactions are subject to specific acid-catalysis, but even in many subject to general acid-catalysis a faster rate was found in deuterium oxide. A slower rate of hydrolysis in deuterium oxide than in water has been found in general acid-catalysed hydrolysis, involving a rate-determining proton-transfer.¹⁶ In the hydrolysis of diisopropyl phosphorofluoridate, general acid-catalysis has been observed by kinetic measurements in buffer solutions.³

Discussion.—The lack of appreciable oxygen-exchange during the hydrolysis of phosphinic fluorides and phosphorofluoridates proves that addition of water to the phosphoryl group cannot be a preliminary fast and reversible step. The observations that hydrolysis is subject to general acid- and general base-catalysis and that it is slightly slower in deuterium oxide seem to indicate that proton-transfer occurs as part of the rate-determining step. The much higher activation energy of diisopropyl phosphorofluoridate than of the phosphorochloridate shows that breakage of the phosphorus-fluorine bond must also be part of the rate-determining step. The less negative entropy of activation of the phosphorofluoridate may be due to unfreezing of water molecules from the hydrogen ions in the transition state.

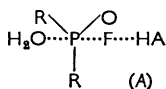
The mechanism which seems best to describe the experimental results is a termolecular "push-pull" mechanism,¹⁷ with the general acid catalyst HA as the electrophilic reagent, and water or some other base as the nucleophilic reagent. The transition state may then be visualised as (A). Other electrophilic reagents, such as chelated Cu(II) may act¹⁸ instead of the acid HA. Alternatively, a two-step mechanism may be proposed for acid-catalysis with rate-determining proton-transfer in the first step, followed by fast addition of water to the phosphorus atom. Such a mechanism does not, however, account for the base-catalysis observed, and for the slight effect of ionic strength.

¹⁵ Reitz, *Z. phys. Chem.*, 1937, **A**, 179, 119; Bell, "Acid-Base Catalysis," Oxford Univ. Press, 1941, pp. 143—152; Lefler and Grunwald in "Technique of Organic Chemistry," Interscience Publ., New York, 1953, Vol. VIII, pp. 319—322; Wiberg, *Chem. Rev.*, 1955, **55**, 713; Pritchard and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 6009; Challis, Long, and Pocker, *J.*, 1957, 4679.

¹⁶ Long, Congress Handbook, XVth Congress Internat. Union Pure Appl. Chem., p. 28, Paris, July 1957; Long and Watson, *J.*, 1958, 2022.

¹⁷ Swain, *J. Amer. Chem. Soc.*, 1950, **72**, 4578.

¹⁸ Courtney, Gustafson, Westerback, Hyytiainen, Chaberek, and Martell, *ibid.*, 1957, **79**, 3030.



EXPERIMENTAL

Materials.—Dimethylphosphinic chloride¹⁹ (3.85 g.), carbon tetrachloride (15 ml.), and sodium fluoride (4.2 g.) were refluxed for 2½ hr. The product was distilled at atmospheric pressure, yielding 1.8 g. (55%) of *dimethylphosphinic fluoride*, b. p. 169—171° (Found: F, 19.2. C₂H₆OFP requires F, 19.8%). The colourless liquid is easily soluble in benzene, chloroform, and *p*-xylene, fairly soluble in water, and only slightly soluble in *n*-hexane.

Diisopropyl phosphorofluoridate was obtained by Saunders and Stacey's method.^{19a}

Diethylphosphinic acid was obtained either by reaction of ethylmagnesium bromide with thiophosphoryl chloride,¹⁹ or by addition of bromine to chlorodiethylphosphine, followed by hydrolysis of the resulting phosphonium chloride: $\text{Et}_2\text{PCl} + \text{Br}_2 = \text{Et}_2\text{PClBr}_2$; $\text{Et}_2\text{PClBr}_2 + 2\text{H}_2\text{O} = \text{Et}_2\text{PO}\cdot\text{OH} + 2\text{HBr} + \text{HCl}$. To chlorodiethylphosphine²⁰ (1.45 g.), a 0.4*N*-solution of bromine in carbon tetrachloride (50 ml.) was added slowly. A white precipitate was formed. Water was added in excess and the mixture was evaporated on the steam-bath. The residual oil was dried at 100° under reduced pressure. To the diethylphosphinic acid formed, benzene (10 ml.) and phosphorus pentachloride (2.4 g.) were added and the mixture was refluxed for 1 hr., then distilled twice under reduced pressure (b. p. 95°/8 mm.), yielding 0.5 g. (31%) of a colourless liquid (Found: Cl, 25.7. Calc. for C₄H₁₀OClP: Cl, 25.3%).

¹⁸O-Enriched water was obtained from the fractionating plant of this Institute. Its ¹⁸O-content was determined by distilling about 0.04 mole of normal carbon dioxide into an evacuated break-seal tube²¹ containing about 0.1 g. of water. The tube was sealed and after storage overnight at 70° for equilibration, the ratio of masses 46 : 44 was determined by a Consolidated Engineering Corporation Model 21-401 mass spectrometer. The atom % concentration of ¹⁸O in the water was calculated from this ratio.²²

Analysis of ¹⁸O in PO·OH Groups.—Di-*p*-tolylcarbodi-imide (0.1 g.; L. Light & Co.) in dry *n*-hexane or ether (4 ml.) was freed from insoluble material by centrifugation. A solution of dialkylphosphinic acid or dialkyl hydrogen phosphate in dry dioxan or ether (5 ml.) was added. Di-*p*-tolylurea crystallised: $2\text{R}_2\text{PO}\cdot\text{OH} + \text{Ar}\cdot\text{N}:\text{C}:\text{N}\cdot\text{Ar} \rightarrow (\text{R}_2\text{PO})_2\text{O} + (\text{Ar}\cdot\text{NH})_2\text{CO}$. Next morning the crystals were centrifuged off, washed several times with dry ether and once with *n*-hexane, and dried under reduced pressure; they had m. p. 277° (reported²⁴ for di-*p*-tolylurea, m. p. 260°). An attempt was made to base the ¹⁸O-determination on the observation that²⁵ di-*p*-tolylurea at 300° decomposes to carbon dioxide, *p*-toluidine, and *NN'*-tri-*p*-tolylguanidine: however, pure di-*p*-tolylurea in evacuated bulbs did not produce carbon dioxide at this temperature. In the presence of small amounts of copper bronze (Triple deep gold bronze powder, Magna Manuf. Co., Inc., N.Y., dried in a hydrogen stream at 300 to 400° for 1 hr.), quantitative decomposition of di-*p*-tolylurea occurred, and the products described by Barr were isolated. Samples of di-*p*-tolylurea (about 30 mg.) with copper bronze (about 1 mg.) were sealed under vacuum in a break-seal tube²⁰ and heated to 320° for 0.5 hr. The carbon dioxide formed was analysed mass-spectrometrically.

Hydrolysis of Dimethylphosphinic Fluoride in ¹⁸O-Enriched Water.—(a) *Complete reaction.* Dimethylphosphinic fluoride (0.135 g.) and enriched water (0.297 g.; 1.17 atom % excess ¹⁸O) were mixed and kept in a thermostat at 25° for 2 hr. The water was then evaporated in a vacuum, and the remaining white crystals of dimethylphosphinic acid were suspended in dry dioxan (1 ml.) and were added to a solution of di-*p*-tolylcarbodi-imide for ¹⁸O-analysis.

(b) *Partial reaction.* Dimethylphosphinic fluoride (0.125 g.) was dissolved in enriched water (10 ml.; 1.17 atom % excess ¹⁸O); after 4 min. chloroform (10 ml.) was added. The mixture was shaken and the layers were separated. The distribution coefficient of dimethylphosphinic acid between water and chloroform had separately been determined as 73 : 1. The chloroform layer was evaporated under reduced pressure and the residue of dimethylphosphinic fluoride was hydrolysed by addition of 1 ml. of normal water. After several hours the water was distilled off in a vacuum-system. The remaining dry dimethylphosphinic acid was dissolved in 1 ml. of

¹⁹ Kabachnik and Shepeleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, **1**, 56; Kosolapoff and Watson, *J. Amer. Chem. Soc.*, 1951, **73**, 5466.

^{19a} Saunders and Stacey, *J.*, 1948, 698.

²⁰ Beeby and Mann, *J.*, 1951, 413.

²¹ Rittenberg and Ponticorvo, *Internat. J. Appl. Rad. Isot.*, 1956, **1**, 208.

²² Dostrovsky and Klein, *Analyt. Chem.*, 1952, **24**, 414.

²³ Khorana and Todd, *J.*, 1953, 2259; Khorana, *Chem. Rev.*, 1953, **53**, 145.

²⁴ Manuelli and Ricca-Rosellini, *Gazzetta*, 1899, **29**, II, 124.

²⁵ Barr, *Ber.*, 1886, **19**, 1768.

dry benzene by gentle warming and was added to a solution of di-*p*-tolylcarbodi-imide in *n*-hexane. Carbon dioxide obtained from the precipitated di-*p*-tolylurea contained 0.01 atom % excess ^{18}O . In the dimethylphosphinic fluoride in the chloroform layer, before its hydrolysis in normal water the content of ^{18}O in the phosphoryl group must have been not more than 0.02 atom % excess.

Hydrolysis of diethylphosphinic chloride was carried out as described in (a). Hydrolysis of diisopropyl phosphorofluoridate was carried out as described in (b), except that *n*-hexane was used as extractant.

Kinetics of Hydrolysis.—The required solutions of the phosphorus fluorides were prepared in volumetric flasks and kept in polyethylene bottles in a thermostat bath. Aliquot parts were withdrawn and analysed for fluoride ions (thorium nitrate and sodium alizarinsulphonate) or for unchanged phosphorus fluoride (hydrogen peroxide and *o*-dianisidine hydrochloride²⁶). Two examples are tabulated.

Hydrolysis of dimethylphosphinyl fluoride (initially 0.008 molar) in water at 24.85°.

Time (sec.)	0	307	560	1088	1500	2294	∞
0.00911N-Th(NO ₃) ₄ (ml.) ...	1.55	2.23	2.48	2.79	3.00	3.60	4.45

From the slope of a plot of $\log(a - x)$ against time, the first-order rate-constant (k_1) was calculated to be $4.0 \times 10^{-4} \text{ sec.}^{-1}$.

Hydrolysis of diisopropyl phosphorofluoridate (initially 0.196 millimolar) in 0.0246M-sodium fluoride at 24.85°. o-Dianisidine method.

Time (hr.)	0	25.5	48	72.3	141.3	164.5	240	313
Optical density ...	0.383	0.290	0.263	0.240	0.141	0.110	0.0775	0.0555

From the slope of a plot of $\log(\text{opt. dens.})$ against time, the first-order rate-constant (k_1) was calculated to be 0.00624 hr.^{-1} .

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²⁶ Marsh and Neale, *Chem. and Ind.*, 1956, 494.