Time at 146–149°	Recovered liquid	n_D^{20}
2 days	60%	1.5468^a
10 days	<10%	1.5463
20 days	<10%	1.5530

^{a} Unreacted styrene n_D^{20} 1.5467 (lit.[9] n_D^{20} 1.5465); polystyrene lit.[9] n_D^{20} 1.59–1.60.

An infrared spectrum showed that the liquid from the two-day ampule was essentially styrene, although traces (<5%) of polystyrene and I were present. Infrared spectra of the products of longer reaction time clearly indicated more polystyrene and I. The liquid products (*ca.* 2 ml.) from several ampules were combined and distilled at 1 mm. from the polystyrene. It was estimated from the refractive index of the distillate that after 10–20 days of reaction the ratio of styrene to I was still *ca.* 10:1. Some of the styrene was removed from the distillate under a vacuum and an infrared spectrum of the residue indicated more definitely the presence of I. The over-all yield of I was <2%.

Acknowledgment. This work was supported by the Office of Ordnance Research.

(9) Boundy and Boyer, *Styrene,* Reinhold Publishing Corp., New York, N. Y., 1952, pp. 57, 216, 450, and 525.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS

Kinetics of Reaction of Acyl Chlorides. III. Hydrolysis of Phosphinyl Chlorides[1]

H. K. HALL, JR.

Recently Dostrovsky and Halmann[2] described a careful study of the kinetics of hydrolysis of dialkyl phosphochloridates, $(RO)_2POCl$. They concluded that these chlorides were prone to react by S_N2 mechanisms even in solvents of high ionizing power. As a continuation of our studies of the mechanisms of hydrolysis of acyl chlorides,[1] it was of interest to extend their study to N,N,N^1,N^1-tetramethylphosphorodiamidic chloride, $[(CH_3)_2N]_2POCl$ (I).

Table I presents the results of the kinetics experiments. I hydrolyzes at a rate almost identical to that of diisopropyl phosphochloridate at 20°. In contrast to the latter, however, the rate of hydrolysis is completely unaffected by added hydroxide ion, *m*-cresoxide ion, or pyrrolidine. This is strong evidence for an S_N1 mechanism of hydrolysis for the former:

$$[(CH_3)_2N]POCl \longrightarrow [(CH_3)_2N]_2\overset{+}{P}{=}O \longrightarrow [(CH_3)_2N]_2P{-}OH$$
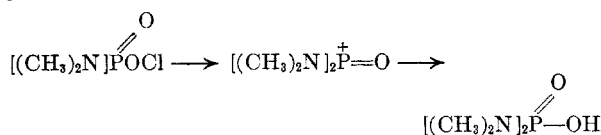
(1) Part II, *J. Am. Chem. Soc.,* in press.
(2) Dostrovsky and Halmann, *J. Chem. Soc.,* 502 *et seq.* (1953).

TABLE I
FIRST ORDER RATE CONSTANTS FOR HYDROLYSIS OF N,N,N^1,N^1-TETRAMETHYLPHOSPHORODIAMIDIC CHLORIDE IN WATER

Initial Conc'n Chloride $\times 10^3$, M.	Temp., °C.	Added Reagents, M	$k_1 \times 10^4$, sec.$^{-1}$
1.093	0.6	NaClO₄, 0.0463	5.05
1.085	15.0	NaClO₄, 0.0463	30.0
1.115	20.1	NaClO₄, 0.0463	52.0
3.09	20.1	NaOH, 0.0206	53.7
4.24	20.1	Pyrrolidine, 0.06425	57.3
1.355	20.1	*m*-Cresol, 0.0416 and NaOH, 0.0416	50.9
1.003	30.0	NaClO₄, 0.0463	141.7

If the reaction were proceeding by an S_N2 mechanism, N,N,N^1,N^1-tetramethylphosphorodiamidic chloride should react much more slowly than diisopropyl phosphochloridate, just as the latter reacts more slowly than diphenylphosphinyl chloride, $(C_6H_5)_2POCl$. Therefore, the hydrolytic rate sequence and the inertness of I to added nucleophiles strongly indicates an ionization mechanism.

In our earlier studies of the mechanisms of hydrolysis of acyl chlorides, it was possible to prove that dimethylcarbamyl chloride[3] and dimethylsulfamyl chloride[1] underwent ionization by trapping the intermediate ions by added nucleophiles. In the present case no products could be isolated which resulted from the reaction of pyrrolidine or *m*-cresoxide ion with the phosphinyl ion. The significance of these contrasting results is not clear. A possible explanation is that the phosphinyl ion is nonlinear, unlike the dimethylcarbamyl and dimethylsulfamyl ions, and that this fact detracts from the resonance stabilization of the ion.

The energy and entropy of activation for the hydrolysis of the alkoxy and dimethylamino derivatives of carbonyl, sulfonyl, and phosphinyl chlorides are presented for comparison in Table II.[4]

Acknowledgments. We are indebted to the Victor Chemical Works for a sample of I, to Dr. P. W. Morgan for helpful advice, and to Mr. Donald G. Preis for excellent technical assistance.

EXPERIMENTAL

Materials and methods. A sample of N,N,N^1,N^1-tetramethylphosphorodiamidic chloride was very kindly furnished by the Victor Chemical Works. It was a water-white liquid, n_D^{30} 1.4625. It contained a very slight deposit of crystalline material. Since we were unable to find published physical properties for this substance, it was analyzed.

(3) Part I, Hall, Jr., *J. Am. Chem. Soc.,* 77, 5993 (1955).
(4) A referee has been kind enough to point out that a plot of $\Delta E\pm$ *vs.* $\Delta S\pm$ is linear for the halides which undergo ionization. The rate constants for these halides are all quite similar in magnitude, however, and this fact may detract from the significance of the relationship.

TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION FOR HYDROLYSIS OF ACYL CHLORIDES

Chloride	Mechanism of Hydrolysis	$\Delta E\ddagger$, Kcal. per mole	$\Delta S\ddagger$, e.u.	Ref.
Ethyl chloroformate	S_N2	19.0	−12.4	3
Dimethylcarbamyl chloride	S_N1	21.6	+ 5.6	3
Methyl chlorosulfonate	S_N1	22.3	+ 7.0	1
Dimethylsulfamyl chloride	S_N1	17.0	−15.0	1
Diethyl phosphochloridate	S_N2	14.4	−22	2
N,N,N¹,N¹-Tetramethylphosphorodiamidic chloride	S_N1	18.8	− 6.7	Present Work

Anal. Calc'd for $C_4H_{12}ClN_2OP$: N, 16.41. Found: N, 16.32, 16.23.

Although the analysis was satisfactory, experimental infinity titers in the rate studies did not always agree satisfactorily with the calculated values. In cases of discrepancy, first order rate constants were calculated by the method of Guggenheim.[5] Rate constants obtained by his method and, in most cases, by conventional first order plots, gave an excellent fit on an Arrnehius plot. The kinetics methods have been described previously.[1,3]

TABLE III

REPRESENTATIVE KINETIC RUN

Initial conc'n I, 1.36×10^{-3} M. Initial conc'n of m-cresol and of sodium hydroxide, 0.0416. Temp., 20.1°C.

Time (min.)	Ml. 0.5166 N HCl	$k_1 \times 10^3$, sec.$^{-1}$
0.72	0.174	5.49
1.09	.250	5.56
1.57	.325	5.35
2.09	.400	5.32
2.85	.485	5.21
3.53	.545	5.14
4.70	.625	5.07
6.40	.720	5.43
30	.821	Av. 5.32

Products of hydrolysis in the presence of pyrrolidine and m-cresol. To a solution of 5.42 g. (0.0762 mole) of pyrrolidine in 1 liter of water at 26° was added with stirring a solution of 5.00 g. (0.0293 mole) of I in 20 ml. of acetone. After 1 hour 25 ml. of 7 M sulfuric acid was added. Continuous extraction of the solution overnight with ether gave no product.

The reaction was repeated exactly as above, using 10.28 g. of m-cresol and 5.9 ml. of 5.2 N sodium hydroxide in place of the pyrrolidine. Continuous ether extraction overnight provided 8.87 g. of m-cresol (86.2% recovery).

(5) Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

PIONEERING RESEARCH DIVISION
TEXTILE FIBERS DEPARTMENT
E. I. DU PONT DE NEMOURS & Co., INC.
WILMINGTON 98, DELAWARE

Kinetics of Reactions of Acyl Halides. V. Reactions of Acyl Chlorides with Substituted Piperidines in Benzene Solution[1]

H. K. HALL, JR., AND P. W. MORGAN

In a study of the mechanisms of hydrolysis of carbonyl chlorides[2] it was found that dimethylcarbamyl chloride hydrolyzed much faster than ethyl chloroformate. This was interpreted as supporting an ionization mechanism for the hydrolysis of the former. It was of interest to compare the reactivities of these two halides under non-ionizing conditions.

The reaction with amines in benzene solution was selected. It was found that dimethylcarbamyl chloride reacted so much more slowly than ethyl chloroformate with a given amine that it was inconvenient to make a direct comparison. Thus the reaction of 0.00248 M ethyl chloroformate with 0.0074 M 2-methylpiperidine was 75% complete in three minutes at 30.0° but the reaction of 0.00648 M dimethylcarbamyl chloride with 0.00957 M 2-methylpiperidine was only 14% complete in 200 minutes.

The great difference in reactivity could be demonstrated indirectly as follows. The hindered base cis-2,6-dimethylpiperidine reacted with ethyl chloroformate at the same rate, within a factor of two, as did the unhindered base piperidine with dimethylcarbamyl chloride. The rate data are given in Table I. The rates showed no discontinuity when the amine began to precipitate, and were identical in stock (0.02% water) and in dry benzene.

Since ethyl chloroformate is more reactive than dimethylcarbamyl chloride in S_N2 reactions of the present type, the opposite rate order for hydrolysis[2] finds satisfactory interpretation in the postulation of an S_N1 reaction for the hydrolysis of the latter.

A brief study of the reaction of benzenesulfonyl chloride with 2-methylpiperidine, and of benzoyl chloride with cis-2,6-dimethylpiperidine, was made. These reactions, unlike those above, exhibited induction periods until salt began to precipitate. The presence or absence of traces of water also influenced these rates. Therefore, these reactions may be mainly heterogeneous.

Acknowledgments. We are indebted to Dr. Caryl Sly for the hydrogenation of 2,6-lutidine and to Mr. Donald G. Preis for excellent technical assistance.

EXPERIMENTAL

Materials. Piperidine, obtained from Matheson-Coleman Bell, was fractionated through a 30 × 1 cm. Vigreux column, b.p. 105.0°.

(1) Part IV, *J. Am. Chem. Soc.*, manuscript submitted.
(2) Part I, Hall, Jr., *J. Am. Chem. Soc.*, **77**, 5993 (1955).