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 Arrhenius 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).

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

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Received November 4, 1955

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).

TABLE I

KINETIC DATA FOR ACYLATION OF AMINES IN BENZENE SOLUTION, 30.0°C.

Acid Chloride	Conc'n $\times 10^3$, M	Amine	Conc'n $\times 10^3$, M	Benzene Solvent	$k_2 \times 10^2$ l. mole^{-1} sec.$^{-1}$
Dimethylcarbamyl chloride	5.67	Piperidine	18.3	Stock	4.95
Dimethylcarbamyl chloride	21.7	Piperidine	43.8	Stock	4.27
Ethyl chloroformate	11.15	*cis*-2,6-Dimethyl-piperidine	21.8	Stock	2.18
Ethyl chloroformate	6.38	*cis*-2,6-Dimethyl-piperidine	31.2	Stock	2.41
Ethyl chloroformate	5.87	*cis*-2,6-Dimethyl-piperidine	22.3	Dry	2.70

cis-2,6-Dimethylpiperidine, b.p. 127.8–128.1°, n_D^{20} 1.4372, was obtained by the hydrogenation of 2,6-lutidine over ruthenium dioxide at 130° and 2000 lb. pressure. *Benzene* was Baker and Adamson Analytical Reagent. Its water content was checked by a Karl Fischer titration.

Acyl chlorides. These were purified as described previously.[2]

Kinetics procedure. Aliquots (5–50 ml.) of standard solutions of the reactants were pipetted into a series of small glass-stoppered separatory-funnels immersed in the bath. Zero time was taken as the moment delivery of the second reactant was begun. At intervals 25 ml. of 0.10 N nitric acid and 25 ml. of chloroform or carbon tetrachloride[3] were added together to a funnel. The mixture was shaken momentarily, the lower organic layer was discarded, and the aqueous layer run into a 125-ml. Erlenmeyer flask. The separatory-funnel was rinsed thoroughly with water, which was added to the aqueous layer. Titration of the aqueous layer for chloride ion was performed by the method of Cavanagh as modified by Dostrovsky and Halmann.[4] When contact was made to the titration solution from a *p*H 3.2 buffer across an unlubricated joint, the results appeared to depend on the acidity of the titration solution. Accordingly a salt bridge (6-mm. tubing, 3% Agar, 5% sodium perchlorate) was used to connect the titration solution to a quinhydrone electrode consisting of a 50-ml. Erlenmeyer flask containing a citrate buffer at *p*H 3.2, quinhydrone, and a platinum wire. The potential was measured with a Beckman model G *p*H meter.

Calculations. For the bimolecular reactions at differing initial concentrations, the following formula was used:

$$\log (a - 2x)/(b - x) = (a - 2b)k_2t/2.30 + \log a/b$$

where a is initial concentration of amine, b is that of acid chloride, and x is that of chloride ion. When the initial concentrations of amine and acid chloride were equivalent or nearly so, the following formula[5] was used:

$$1/(d - x) - 1/d = 2k_2t, \text{ where } \frac{a}{2} - s = d,\ b + s = d,$$

where s is the difference between a and b.

(3) By using solvents denser than water, the hydrolyzable acid chloride is removed in the first separation.

(4) Dostrovsky and Halmann, *J. Chem. Soc.*, 506 (1953).

(5) See Frost and Pearson, *Kinetics and Mechanism*, John Wiley and Sons, Inc., New York, 1953, p. 19.

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Preparation of 2-Hydroxyethylammonium Acetate

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Received October 14, 1955

In the course of preparing N-acetylethanolamine (I) in this laboratory, the reaction between acetic anhydride and ethanolamine was investigated. According to Jones[1] the reaction of acetic anhydride and ethanolamine in methanol solution gave a 97% yield of I upon distillation of the product under reduced pressure. We have found, following his technique, that the product consists of an equimolecular mixture of I and the previously unreported 2-hydroxyethylammonium acetate (II).

$$(CH_3OO)_2O + 2\,NH_2CH_2CH_2OH \rightarrow CH_3CONHCH_2CH_2OH \text{ (I)} + CH_3COO\bar{H}_3\overset{+}{N}CH_2CH_2OH \text{ (II)}$$

Upon distillation at reduced pressure the lower-boiling II is easily separated from I and crystallizes on standing to a hydroscopic, low-melting, solid. On further heating II is converted to I, but only under conditions such that II cannot distill. Vacuum distillation of an equimolecular mixture of acetic acid and ethanolamine, without prior heating, gives a quantitative yield of II.

The isolation of II in this way is surprising in view of a preparation of I by Wenker[2] which consists of merely heating glacial acetic acid and ethanolamine at atmospheric pressure until the stoichiometric amount of water is evolved and then distilling under a vacuum. (A duplication of Wenker's technique gave I in excellent yield). The amide-forming reaction begins at about 160° and is completed when the temperature of the mixture reaches 200–220°. Thus, if the crude product obtained by Jones[1] is distilled at the pressure he re-

(1) Jones, *J. Org. Chem.*, 9, 484 (1944).

(2) Wenker, *J. Am. Chem. Soc.*, 57, 1079 (1935).