[Contribution from the Department of Chemistry of the Polytechnic Institute of Brooklyn]

Reactions of Alkyl Halides with Silver Nitrate in Pyridine[1]

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The kinetics of the reactions of primary and secondary chlorides in pyridine with the solvent and with silver nitrate were measured at 68.8°. The primary chlorides were more reactive than the secondary compounds for both reactions. Similar effects were found for primary and secondary bromides at 27.6°. Within the limits of experimental error, water, methanol, phenol and silver chloride have no effect on the rate of either reaction. Various salts accelerated both reactions. It is concluded that the solvent reaction, a direct nucleophilic displacement by pyridine, may be assisted by the electrophilic silver ion without changing the mechanism.

Introduction

This research was concerned primarily with the reactions of alkyl halides with silver nitrate in pyridine, selected as solvent for two reasons. Previous studies of silver salt reactions with these compounds have been complicated by heterogeneous catalysis due to the precipitated silver halide.[2–6] This problem does not arise in pyridine, in which both silver chloride[7] and silver bromide are quite soluble. In addition, most previous studies of these reactions were conducted in solvents like water or ethanol, which themselves are capable of reacting with the organic halides by the same mechanism as the silver salt reactions, *i.e.*, SN1. The present research involves a distinct contrast in mechanism of reaction between solvent and silver nitrate, in that the former unquestionably reacts with the organic halides by nucleophilic displacement (SN2) rather than by the electrophilic attack of the silver ion (SN1). It was felt that the interplay of mechanisms of different types might provide additional information about these reactions.

An important part of the driving force of the alkyl halide–silver ion reaction is the formation of silver halide, which is only weakly dissociated in pyridine.[8]

The reactions between pyridine and alkyl and aralkyl halides have been extensively investigated in many solvents, but there has been no previous report of studies carried out in pyridine itself. It was necessary in this work to distinguish the reaction between solvent and halide from that among solvent, halide and silver salt. Accordingly, *n*-butyl chloride, *sec*-butyl chloride, *n*-octyl chloride and *sec*-octyl chloride were allowed to react in pyridine at 68.8° in the presence and absence of silver nitrate, while *n*-butyl bromide and *sec*-butyl bromide were studied in similar fashion at 27.6°.

Experimental

Reagents.—Benzene was a reagent grade product dried over sodium and distilled. The middle portion was collected and redistilled; b.p. 79–80°. Butene-1 was a reagent grade product of Matheson, Coleman and Bell. *n*-Butyl bromide was a C.P. product twice distilled from anhydrous potassium carbonate; b.p. 101–102°. *sec*-Butyl bromide, treated in similar fashion, boiled at 91–92°. *n*-Butyl chloride was a Carbide and Carbon Chemical Co. product which was treated with concentrated sulfuric acid and distilled; b.p. 77–78°. The secondary compound was a C.P. material which was purified in the same way; b.p. 68–69°. *n*-Butyl nitrate was prepared by treating *n*-butyl iodide with silver nitrate; b.p. 134–135°. *n*-Butylpyridinium chloride was prepared by refluxing *n*-butyl chloride with an excess of pyridine for 24 hours. The solid was washed with ether and dried *in vacuo;* m.p. 124–131°. Nitron was a Fisher Scientific Co. product which was recrystallized from ethanol. *n*-Octyl chloride was prepared by treating *n*-octyl alcohol with thionyl chloride in ether. The product was fractionally distilled, washed with concentrated sulfuric acid, and redistilled; b.p. 181–182°. The secondary compound was prepared by treating octanol-2 with phosphorus pentachloride, and purified; b.p. 172–173°. Pyridine was a Barrett Division product. It was dried for at least two weeks over fused potassium hydroxide, and fractionally distilled three times; b.p. 115–116°. Analysis of the pyridine by Karl Fischer titration[9] showed that there was 0.031% water by weight. Pyridine nitrate was prepared by treating pyridine with concentrated nitric acid. The resulting white solid was recrystallized from ethanol. Silver chloride was prepared by adding hydrochloric acid to an aqueous solution of silver nitrate and washing the precipitate thoroughly with hot water, drying it at 100°. It was stored in the dark. Silver nitrate was a Mallinckrodt reagent grade product, and was used without further purification. Tetra-*n*-butylammonium nitrate was prepared by the method of Fuoss, Cox and Kraus.[10] Thionyl chloride was redistilled from the Matheson, Coleman and Bell product; b.p. 76–77°. Wijs reagent was obtained from the Fisher Scientific Co.

Kinetic Procedure.—The reaction solutions were prepared by weighing out appropriate quantities of the alkyl halide from a weight buret into a volumetric flask and diluting to the mark with pyridine. Ten-ml. portions of the solutions were pipetted into test-tubes which were sealed after freezing in a Dry Ice–solvent mixture. The tubes were allowed to come to equilibrium at room temperature and then immersed in a constant temperature bath which operated at the desired temperature ±0.1°. Zero time was the time at which the tubes were placed in the bath. One of the tubes in each series was analyzed immediately after sealing in order to determine the extent of any initial reaction.

At suitable times a tube was removed from the bath and frozen in a Dry Ice–solvent mixture. It was then opened and the contents were treated with 100 ml. of water and 100 ml. of benzene. The mixture then was placed in a separatory funnel and the lower water layer was removed. The benzene layer was washed with approximately 25 ml. of water and this was added to the first water extract. To this water layer was added an excess of silver nitrate to ensure complete precipitation of all ionized halide. The mixture was acidified with nitric acid and the silver chloride (or silver bromide) precipitate was determined gravimetrically. Appropriate blanks showed that the loss of chloride was less than 1%.

For solutions containing silver nitrate, the reactions were run until crystals of silver chloride appeared in the specimen tubes which corresponded usually to form 50 to 90% of com-

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(1) From the Ph.D. thesis of Joseph A. Vona, 1954.

(2) K. A. Burke and F. C. Donnan, *J. Chem. Soc.*, 555 (1904).

(3) K. A. Burke and F. C. Donnan, *Z. physik. Chem.*, **69**, 148 (1909).

(4) F. C. Donnan and H. E. Potts, *J. Chem. Soc.*, 1882 (1910).

(5) H. Euler, *Ber.*, **39**, 2726 (1906).

(6) G. Senter, *J. Chem. Soc.*, 347 (1919).

(7) L. Kahlenberg and W. J. Wittick, *J. Phys. Chem.*, **13**, 421 (1908–1909).

(8) J. H. Matthews and A. J. Johnson, *ibid.*, **21**, 294 (1916–1917).

(9) J. D. Neuss, M. G. O'Brien and H. A. Frediani, *Anal. Chem.*, **23**, 1332 (1951).

(10) R. M. Fuoss, N. L. Cox and C. A. Kraus, *Trans. Faraday Soc.*, **31**, 949 (1935).

pletion. In some instances, the runs were continued beyond this point. Values of the rate constant corresponding to the two-phase system were not included in the calculations. The samples were treated with 100 ml. of 15% ammonium hydroxide and 100 ml. of benzene. The water layer was acidified with nitric acid, and the resulting precipitate was weighed.

Analysis of Reaction Products. Olefins.—One hundred ml. of 0.1 *M* solutions of the halide and silver nitrate in pyridine were allowed to react practically to completion at the temperature of the kinetic runs. Carbon dioxide was blown through the sample and passed through traps cooled with ice and with Dry Ice into two flasks in series containing known quantities of Wijs reagent. After 7 hours of gas collection, the Dry Ice was removed to permit reaction between olefin and the Wijs reagent. Appropriate blanks were run on the reagent with standardized sodium thiosulfate solution. The procedure was checked with known quantities of butene-1. Typical results are

Butene-1 taken, g.	Butene-1 recovered, g.
0.018	0.017
.382	.385
.70	.66

Additional blanks showed no reaction between silver nitrate and butene-1 in pyridine.

Quaternary Salts.—A liter of pyridine solution 0.1 *M* in alkyl halide and in silver nitrate was maintained at the appropriate temperature to complete reaction. The bulk of the pyridine was removed under reduced pressure below 30°, water was added, and solids were removed by filtration. Dissolved silver was precipitated from the filtrate with hydrochloric acid. The solution after filtration was diluted to a known volume, and an aliquot was passed through an ion-exchange column of Dowex-1 in the hydroxyl state, giving an eluate containing N-alkylpyridinium hydroxide and residual pyridine. An aliquot of the eluate was titrated with standardized hydrochloric acid to a methyl orange end-point (a procedure which permitted determination of the quaternary hydroxide in the presence of the weak base pyridine). The analyses of known samples of N-butylpyridinium chloride were satisfactory. The reproducibility was better than 1%.

Nitrate Esters.—Nitrate esters were determined by the method of Busch.[11] Solutions 0.1 *M* in *n*-butyl chloride (or *sec*-butyl chloride) and 0.1 *M* in silver nitrate in pyridine were allowed to react to completion at 68.8°. After extraction of the cooled mixture with benzene and ammonia, the benzene layer was boiled with 0.5 *M* alcoholic potassium hydroxide and distilled. The dry residue was examined for nitrate ion (as potassium nitrate) by addition of nitron reagent. Blanks run with *n*-butyl nitrate showed 98% recovery.

Results and Discussion

Analysis of Reaction Products.—With *n*-butyl chloride and silver nitrate in pyridine for three days at 68.8°, analysis of silver chloride showed that the reaction had proceeded 78% toward completion. Analysis for quaternary salt showed a 77% yield. Neither olefin nor nitrate ester was found. It is assumed that in the absence of silver nitrate, as in its presence, quaternary salt was the only reaction product. In this connection, appropriate blanks on *n*-butylpyridinium chloride in pyridine at 68.8° showed that there was no reverse reaction.

With *sec*-butyl chloride and silver nitrate in pyridine for 27.1 days at 68.8°, 83% of the theoretical amount of silver chloride was found. Analysis for quaternary salt showed a 75% yield. A small amount (7.3%) of olefin was formed, but no nitrate ester was detected. In a run with *sec*-butyl chloride in pyridine, essentially the same results were obtained. It can therefore be concluded that the secondary chloride reacted with pyridine to yield about 90–92% quaternary salt and 8–10% olefin, whether silver nitrate was present or not. This is contrary to previously reported studies in other solvents.[2,3]

Kinetic Data. (1) Reaction with Solvent.—The change in concentration of the *n*-alkyl halides with time was adequately represented by the usual first-order expression

$$k = (1/t)\ 2.3 \log a/(a - x) \qquad (1)$$

which was used to calculate the rate constant k. There was a small increase in k as the reaction proceeded, due probably to a positive salt effect by the quaternary salt formed.

For the secondary halides, since the yield of olefin was 10% or less, the elimination reaction was ignored in the calculations of the first-order rate constants. For them too there was a small upward drift in the velocity constants as the reaction proceeded. Typical data are shown for both *n*-butyl and *sec*-butyl chloride in Table I.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR *n*-BUTYL CHLORIDE AND *sec*-BUTYL CHLORIDE IN PYRIDINE AT 68.8°

n-Butyl chloride (107.4 m*M*)				*sec*-Butyl chloride (205.6 m*M*)			
Time, hr.	x	$a - x$	10_4k, hr.$^{-1}$	Time, hr.	x	$a - x$	10^4k, hr.$^{-1}$
8	12.3	141.6	102	43.5	4.4	290.5	4.3
20	28.9	125.0	104	144	19.3	275.6	4.8
26	36.9	117.0	106	288	39.1	255.8	4.8
47	63.1	90.8	113	552	63.4	231.5	4.4
57	73.1	80.8	115	792	103.6	191.3	5.4
66	81.6	72.3	115	1032	129.0	165.7	5.6
72	87.6	66.3	117	1368	162.2	132.7	5.6
143	127.1	26.8	121	2544	238.6	56.3	6.5
			112 ± 6				5.2 ± 0.6

A summary of the results of the kinetic data on runs at 68.8° is presented in Table II.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR REACTIONS OF BUTYL AND OCTYL CHLORIDES AT 68.8°

Compound, chloride	Concentration, mmoles/liter	10^4k, hr.$^{-1}$
n-Butyl	125.7	111 ± 3
	107.4	112 ± 6
	224.8	115 ± 6
	219.2	113 ± 8
sec-Butyl	110.3	5.0 ± 0.3
	205.6	5.2 ± .6
	196.4	5.5 ± .6
n-Octyl	103.5	116 ± 2
	207.8	122 ± 11
	204.2	120 ± 10
sec-Octyl	103.4	4.4 ± 0.1
	225.9	4.5 ± 0.3

The effects of water on the solvent reaction of *n*-butyl chloride were examined. The results are given in Table III, together with the effects of several other substances.

It has been concluded that water has no effect on the solvent reaction of *n*-butyl chloride, and that phenol and methanol, which have been reported to exert catalytic action in a reaction between an amine and an aralkyl chloride,[12] play no such part

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(11) M. Busch, *Ber.*, **38**, 861 (1905).

(12) C. G. Swain, THIS JOURNAL, **70**, 1119 (1948)

TABLE III

EFFECTS OF WATER AND OTHER HYDROXYLIC SUBSTANCES ON THE SOLVENT REACTION OF *n*-BUTYL CHLORIDE AT 68.8°

Initial concentration of *n*-butyl chloride, mmoles/liter	Additive	Concentration, mmoles/liter	10^4k, hr.$^{-1}$
107.4	None	. .	112 ± 6
110.2	Water	50	116 ± 5
105.7	Phenol	100	107 ± 3
97.8	Methanol	95	108 ± 2

here. For *sec*-butyl chloride also, water had virtually no effect on the solvent reaction.

(2) **Reactions with Silver Nitrate. (A) Calculations of Second-order Rate Constants.**—Preliminary experiments showed that the addition of silver nitrate caused an increase in the rate of reaction of the alkyl chlorides in pyridine. Measurements of the kinetics of the reactions were interpreted in terms of an apparent second-order reaction added to an apparent first-order (*i.e.*, solvent) reaction

$$\mathrm{RCl} + \mathrm{C_5H_5N} \longrightarrow \mathrm{C_5H_5NR^+Cl^-} \qquad (2)$$

$$\mathrm{RCl} + \mathrm{AgNO_3} + \mathrm{C_5H_5N} \longrightarrow \mathrm{C_5H_5NR^+NO_3^-} + \mathrm{AgCl} \qquad (3)$$

The rate equation for such a system is

$$-\mathrm{d(RCl)}/\mathrm{d}t = k_1(\mathrm{RCl}) + k_2(\mathrm{RCl})(\mathrm{AgNO_3}) \qquad (4)$$

The general solution to this equation is

$$t = \frac{1}{k_1 - k_2(\mathrm{RCl})_0 + k_2(\mathrm{AgNO_3})_0} \ln \frac{k_1 + k_2(\mathrm{AgNO_3})k_2(\mathrm{RCl})_0}{k_2(\mathrm{RCl})(k_1 + k_2[\mathrm{AgNO_3}]_0)} \qquad (5)$$

in which the zero subscript refers to the initial concentration of the particular reacting species. Calculation of rate data from this equation is quite laborious. Accordingly, the practice of some earlier workers[13] was adopted in which the initial concentrations of the two reacting species are made equal (or nearly so) with the consequence that the equation is simplified

$$k_2 = \frac{k_1}{(\mathrm{RCl})_0(\mathrm{RCl})}\left[\frac{(\mathrm{RCl})_0 - (\mathrm{RCl})e^{k_1t}}{e^{k_1t} - 1}\right] \qquad (6)$$

Table IV shows data for the reactions at 68.8°, calculated according to equation 6.

It can be seen that the second order rate constant is substantially the same over a three-fold concentration range for any particular chloride. There was a small upward drift in the constants for the primary chlorides as the reaction proceeded, but there was no detectable trend for the secondary compounds.

The possible catalytic effect of dissolved silver chloride on the reaction was investigated in the presence and absence of silver nitrate. The results are shown in Table V.

It was concluded that dissolved silver chloride exerted no catalysis on the rate of either the solvent reaction or the reaction with silver nitrate.

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR THE REACTIONS OF SILVER NITRATE WITH ALKYL CHLORIDES AT 68.8°, CALCULATED ACCORDING TO EQUATION 6

Compound, chloride	Concentration, mmoles/liter	Concn. of silver nitrate, mmoles/liter	10^3k, l.-mole^{-1} hr.$^{-1}$
n-Butyl	45.6	46.6	122 ± 11
	91.4	93.4	134 ± 12
	140.6	142.0	120 ± 8
	146.7	151.2	130 ± 13
	152.9	153.4	134 ± 7
n-Octyl	51.3	51.9	136 ± 11
	155.9	154.9	130 ± 12
sec-Butyl	58.6	59.7	36 ± 1
	55.7	56.1	32 ± 1
	156.6	154.9	32 ± 2
	150.9	152.8	33 ± 2
	149.7	150.2	33 ± 1
sec-Octyl	55.1	57.0	26 ± 3
	182.6	187.5	30 ± 1

TABLE V

THE EFFECT OF DISSOLVED SILVER CHLORIDE ON THE REACTIONS OF PRIMARY AND SECONDARY BUTYL CHLORIDES IN PYRIDINE AT 68.8°

Concentration, mmoles/liter	Concn. of $AgNO_3$, mmoles/liter	Concn. of AgCl, mmoles/liter	10^4k (eq. 1)	10^3k (eq. 6)
		n-Butyl chloride		
107.4	0	0	112 ± 6	
98.1	0	14	114 ± 2	
104.8	0	28	116 ± 4	
106.1	0	42	118 ± 3	
152.9	153.4	0		134 ± 7
147.5	159.4	19.4		134 ± 3
148.6	154.4	43.0		133 ± 6
370.7	379.4	41.0		134 ± 2
369.1	375.1	13.1		132 ± 8
		sec-Butyl chloride		
196.4	0	0	5.5 ± 0.6	
99.6	0	34.5	5.4 ± 0.2	
150.9	152.8	0		33 ± 2
153.4	154.3	35.7		30 ± 1

In similar fashion, it was found that water (up to 77.3 mmoles/liter) had a negligible effect on the rate of the reaction between silver nitrate and *n*-butyl chloride, and (up to 55 mmoles/liter) had a small effect on the reaction between *sec*-butyl chloride and silver nitrate.

B. Considerations Regarding Salt Effects.—A second method of interpreting the experimental data from the samples containing silver nitrate is to assume that the silver nitrate is simply exerting a salt effect on the reaction between the alkyl chloride and pyridine. In order to consider this interpretation more fully, a number of experiments were conducted on the effects of various dissolved salts on the kinetics of the solvent reaction. The data, together with first-order constants recalculated according to equation 1 from the runs with silver nitrate, are presented in Table VI.

The first conclusion drawn from these data is that there are positive salt effects on the solvent reactions of both the primary and secondary chlorides. This is not unexpected, since the transition state of the reaction with pyridine probably involves some charge separation. Further, the effects of nitrates (other than silver) appear to be greater with the secondary compound, consonant

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[13] V. K. LaMer and J. Greenspan, THIS JOURNAL, **56**, 1493 (1934).

TABLE VI

EFFECTS OF SALTS ON THE FIRST-ORDER VELOCITY CONSTANTS OF THE BUTYL CHLORIDES AT 68.8°

Chloride	Concn., mmoles/liter	Salt	Concn., mmoles/liter	10^4k, hr.$^{-1}$
n-Butyl	219.2	None	0	113 ± 8
	199.5	Pyridinium nitrate	200.2	137 ± 2
	200.8	Tetra-*n*-butylammonium nitrate	200.9	166 ± 2
	45.6	Silver nitrate	46.6	150 ± 20
	91.4	Silver nitrate	93.4	210 ± 10
	140.6	Silver nitrate	142.0	250 ± 10
	152.9	Silver nitrate	153.4	280 ± 10
	213.5	Silver nitrate (+80 mmoles H_2O)	204.8	320 ± 10
sec-Butyl	205.6	None	0	5.2 ± 0.6
	207.3	Pyridinium nitrate	199.7	7.5 ± 0.2
	207.1	Tetra-*n*-butylammonium nitrate	207.4	9.9 ± 0.5
	58.6	Silver nitrate	59.7	26 ± 1
	150.9	Silver nitrate	152.8	50 ± 5

with a greater charge separation in the transition state. However, effects of silver nitrate on the kinetics of the reaction, considered simply as salt effects, are much larger than the effects of the other nitrates. In this connection, if the supposed salt effect is treated in a very simplified fashion in accordance with the equation

$$k = k_0(1 + A\ [\text{salt}]) \qquad (7)$$

in which k represents the experimental velocity constant in the presence of the salt, k_0 is the velocity constant in solvent alone, A symbolizes the normalized effect of a particular salt and the salt term in brackets stands for the concentration of the particular salt, then the following table shows the normalized salt effects of the various electrolytes (including silver nitrate), together with the dissociation constant for each electrolyte in pyridine at 25°,[14-18] calculated from conductance data.

TABLE VII

KINETIC SALT EFFECTS AND DISSOCIATION CONSTANTS IN PYRIDINE

Chloride	Salt	10^3A, eq. 7	$10^4 \times$ *K*diss.
n-Butyl	Pyridinium nitrate	12	0.51
	Tetra-*n*-butylammonium nitrate	17	3.7
	Silver nitrate	100	9.3
sec-Butyl	Pyridinium nitrate	1.2	0.51
	Tetra-*n*-butylammonium nitrate	2.4	3.7
	Silver nitrate	29	9.3

While it is true that the positive kinetic salt effect for a particular nitrate seems to be related in a general way to its dissociation constant, the apparent effect of silver nitrate is much greater than one would expect from its dissociation constant. Thus, tetra-*n*-butyl nitrate exerts a salt effect on *n*-butyl chloride which is 50% greater than that of pyridinium nitrate, whereas its dissociation constant (at room temperature) is six times greater. Silver nitrate, whose dissociation constant is eighteen times greater than that of pyridinium nitrate, exerts a salt effect which is more than eight times that of pyridinium nitrate. These numbers are approximately doubled for the secondary chloride. Because of the disproportionately large effect of silver nitrate compared to the other nitrates, it is concluded that it is exerting a catalytic effect in addition to a possible salt effect (of perhaps the same order as that of tetra-*n*-butylammonium nitrate). This conclusion is supported by additional considerations. The *n*-butyl chloride in the presence of silver nitrate reacts more rapidly than in solvent alone, but the two rates are still comparable with one another. Calculation of an apparent first-order constant according to equation 1 shows no downward trend in the value of the constant as the reaction proceeds. The *sec*-butyl chloride in the presence of sufficient silver nitrate, however, reacts so much more rapidly than in solvent alone that one can effectively ignore the solvent reaction. With most of the *sec*-butyl chloride runs in silver nitrate solution, calculation of a first-order constant shows a decided downward trend in the value of the constant as the reaction proceeds. This is an effect which is to be expected if too low an order has been selected for kinetic calculations. In addition, several runs were made with alkyl chloride, silver nitrate and tetra-*n*-butylammonium nitrate. In the case of the *n*-butyl compound, the addition of tetra-*n*-butylammonium nitrate resulted in an increase in the first-order rate constant calculated according to equation 1, but no significant change in the second-order constant calculated according to equation 6. With the *sec*-butyl compound, the addition of the quaternary nitrate resulted in no change in the first-order constant or in the second-order constant. If the effect of silver nitrate is simply a salt effect, adding other electrolyte to the system should increase the value of the first-order constant. On the other hand, if its effect is primarily catalytic, the addition of neutral electrolyte should have virtually no effect on the rate of the reaction, since there is probably no redistribution of charge in the transition state for the catalyzed reaction. As silver ion pulls the chloride away, the quaternary ion begins to form.

C. Kinetics of Reaction of Primary and Secondary Butyl Bromides in Pyridine.

—Similar experiments were performed with normal and secondary butyl bromides at 27.6°. With the normal compound, because of its reactivity with pyridine, a zero time correction was determined, and applied to each run. The results are given in Table VIII.

It can be seen that the same general trends apply here which were noted in the chloride systems. The reactivity of the primary compound to pyridine is roughly twenty times greater than that of the secondary, and its reactivity to silver nitrate is about five times greater. The second order con-

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(14) E. A. Anderson, *J. Phys. Chem.*, **19**, 753 (1914-1915).

(15) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

(16) D. L. Fowler and C. A. Kraus, *ibid.*, **62**, 2237 (1940).

(17) W. F. Luder and C. A. Kraus, *ibid.*, **69**, 2481 (1947).

(18) D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 707 (1948).

Table VIII

Kinetics of Reaction of Butyl Bromides in Pyridine at 27.6°

Bromide	Concn., mmoles/liter	Silver nitrate concn., mmoles/liter	10^3k, hr.$^{-1}$ acc. to eq. 1	10^3k, l.-mole^{-1} hr.$^{-1}$, acc. to eq. 6
n-Butyl	96.1	0	57 ± 1	
	46.4	49.3	85 ± 6	786 ± 23
	103.8	104.7	108 ± 10	737 ± 64
	132.7	136.3	117 ± 11	771 ± 140
sec-Butyl	102.6	0	2.5 ± 0.1	
	46.8	47.3	7.5 ± .6	147 ± 5
	103.9	104.4	13 ± .3	150 ± 3
	147.3	148.6	18 ± 3	157 ± 2

stant is practically the same over a threefold concentration range of halide and silver nitrate. In addition, with both bromides, calculation of first-order constants for the silver nitrate solutions resulted in markedly decreasing values of the constants as reaction proceeded. No trend was discernible in the values of the corresponding second order constants.

It is concluded that silver nitrate is reacting with the alkyl halides in pyridine. The primary compounds react with pyridine alone approximately twenty times more readily than the secondary halides. This is not unexpected for an S$_N$2 reaction. Furthermore, the primary compounds react five times more rapidly with silver nitrate than the secondary halides, again as expected for a direct nucleophilic displacement which now has electrophilic assistance. In the solvent reaction, pyridine is, of course, a strong nucleophile but may also act as a weak electrophile, solvating the ion-pair which is being formed. Silver ion is, of course, a much more effective electrophile. In the present system it appears that "push" by the pyridine is more important than "pull" by the silver ion. This conclusion emerges from both the kinetic results and the analyses of the products of the reactions, in which the yields of olefin and quaternary salt were unchanged by the addition of silver nitrate.

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Brooklyn 1, N. Y.

[Contribution from the School of Chemistry of the University of Minnesota]

Reaction of 1-Iodomercuri-2-propanol and its Methyl Ether with Non-halogen Acids[1]

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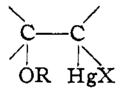
The reaction of $CH_3CH(OR)CH_2HgI$ with perchloric and acetic acids has been examined for R = H and R = CH_3. The products are propylene, HgI_2, HOR and $CH_3CHORCH_2Hg^{\oplus}$ (the latter either as the perchlorate or the acetate). The reaction rate is proportional to the hydronium ion concentration in dilute solution and is independent of the concentration of molecular acetic acid. For both R = H and R = CH_3, the reaction is faster in D_2O than in H_2O. These facts suggest very strongly that the first step in this reaction is a fast, reversible protonation of the substrate oxygen and that this is followed by a rate-determining step in which no covalent bonds to solvent or acetate ion are formed. The exact nature of the rate-determining step and the structure of the transition state are not yet known.

It has long been known that compounds of the general type I, where R is either a hydrogen atom or an alkyl group and X is a halogen atom, generate



Ia, R = H, X = I
Ib, R = CH_3, X = I

the corresponding olefin on treatment with halogen acids and sometimes also on treatment with acetic acid.[2] Several mechanisms have been proposed for this reaction,[3,4] but none seems to have been definitely established. In the present paper the stoichiometry and kinetics of the reactions with aqueous perchloric and acetic acid are reported, along with the effect on the rate of changing the solvent to D_2O. Solvent and salt effects are also briefly reported. Considerable information about the mechanism of the reaction is deduced.

Results

Products.—All of the results are consistent with the stoichiometry shown in eq. 1. On treatment

$$2CH_3CH(OR)CH_2HgI + H_3O^{\oplus} \longrightarrow CH_3CH{=}CH_2 + H_2O + CH_3CH(OR)CH_2Hg^{\oplus} + ROH + HgI_2 \quad (1)$$

$$CH_3CH(OR)CH_2HgI + H_3O^{\oplus} \longrightarrow CH_3CH{=}CH_2 + H_2O + HgI^{\oplus} + ROH \quad (2)$$

$$CH_3CH(OR)CH_2HgI + HgI^{\oplus} \longrightarrow CH_3CH(OR)CH_2Hg^{\oplus} + HgI_2 \quad (3)$$

$$R = H \text{ or } CH_3$$

with a large excess of 0.2 *M* aqueous perchloric acid, 3.49 mmoles of Ia produced 1.84 mmoles of gas (assumed to be propylene). Similarly 3.96 mmoles of Ib produced 2.03 mmoles of gas. It was shown that Ia produced no significant quantity of isopropyl alcohol, precluding an electrophilic displacement reaction.

The spectra of HgI_2 and $HgI^{\oplus}$ have been previously determined.[5] Redetermination gave good agreement in the case of HgI_2, but in the case of $HgI^{\oplus}$ the previously reported valley around 2500 Å. was partially filled in.[6] With both

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[1] Presented in part at the April, 1958, Meeting of the American Chemical Society, San Francisco, Calif.

[2] (a) F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1921, Chap. V. (b) G. F. Wright, *Ann. New York Acad. Sci.*, **65**, 436 (1957). (c) J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[3] A. Rodgman, D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **35**, 1377 (1957).

[4] F. C. Whitmore, *Chem. Eng. News*, **26**, 672 (1948).

[5] M. M. Kreevoy, This Journal, **79**, 5929 (1957).

[6] The argument for the products of acid cleavage of CH_3HgI (ref. 4) are strengthened by the new spectrum for $HgI^{\oplus}$.