tions chiefly, and this was borne out by the oxidation of 2 g. of the first fraction (b. p. 122° at 3–4 mm.), when 0.420 g. of the dibasic acid, m. p. 140.5–141.5° (corr.), was obtained.

Titrations of the dibasic acid with 0.0602 N sodium hydroxide, with phenolphthalein as indicator, gave the acid equivalent of 130.8, whereas that calculated is 131.

Summary

1. The dehydration of β-phenylethyl-3-methylcyclohexanol-1 by 85% sulfuric acid gives chiefly 2-methyloctahydrophenanthrene, with small amounts of 3-methylspirocyclohexane-1,1-indan.

2. The 2-methyloctahydrophenanthrene was identified by dehydrogenation to the 2-methylphenanthrene, and the spirane by oxidation to the corresponding homophthalic acid.

3. A new route has been opened to 2-methylphenanthrene.

4. An oxidation method has been developed for detecting the presence of small amounts of spiro-indans in a mixture containing octahydrophenanthrenes.

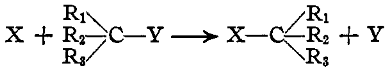
NEW YORK, N. Y. RECEIVED OCTOBER 13, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Walden Inversion: Configurational Effects in the Solvolytic Reactions of α-Phenylethyl Chloride[1]

BY JOSEPH STEIGMAN AND LOUIS P. HAMMETT

It is extremely probable that all bimolecular substitution reactions of the type



$$X + \begin{matrix}R_1\\R_2\\R_3\end{matrix}\!\!>C-Y \longrightarrow X-C\!\!<\begin{matrix}R_1\\R_2\\R_3\end{matrix} + Y \qquad (1)$$

take place with inversion of configuration in such a way that the configuration, of the product $XCR_1R_2R_3$ is the mirror image of that of the reactant $R_1R_2R_3CY$. This conclusion finds most emphatic support on the empirical side from the brilliant investigations of Kenyon and Phillips[2] on the reactions of toluene-sulfonates; on the theoretical side Polanyi[3] and Olson[4] have shown that it is a necessary result of London's[5] quantum mechanical interpretation of the substitution process. For the particular case of the reaction of an organic halide with halide ion its validity has been conclusively demonstrated by the work with the radioactive iodine isotope of Hughes, Juliusberger, Masterman, Topley and Weiss.[6] For reactions of this type, therefore, the relative configurations of reactant and product are known with a high degree of certainty. It therefore becomes the most important task of research in this field to determine whether other types of substitution also effect a change in configuration. Such investigations, if successful, will reduce the Walden Inversion to a problem in reaction mechanism, accessible to study by the methods of reaction kinetics.

From this point of view it is apparent that, in the beginning at least, the reactions to be investigated must be fundamental one-step reactions; they must be Urreaktionen in the sense of Skrabal.[7] Clearly if a reaction consists of two or three or more successive steps, the final configuration will be inverted or not according as the number of steps involving inversion is odd or even.[2,4] Consequently the reactions of the halogen and hydroxy derivatives of acids must be recognized as most difficult material for this kind of investigation in spite of the success of Olson's[8] analysis in certain cases. One need only glance at Dawson and Dyson's[9] thoroughgoing study of kinetics and mechanism in the hydrolysis of bromoacetic acid or Long and Olson's[10] study of the reactions of bromosuccinate ion to realize what a complicated system of parallel complex reactions may appear in such a case, and to understand why so much of the mystification which has always surrounded the Walden inversion arises from the unlucky fact that the acid derivatives are the most easily accessible optically active substances.

Confining our attention then to alkyl halides

---

[1] Based upon the dissertation submitted by Joseph Steigman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Kenyon and Phillips, *Trans. Faraday Soc.*, **26**, 451 (1930).

[3] Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

[4] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[5] London, *Z. Elektrochem.*, **35**, 552 (1929).

[6] Hughes, Juliusberger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935).

[7] Skrabal, *Monatsh.*, **64**, 289 (1934).

[8] Olson and Long, THIS JOURNAL, **56**, 1294 (1934).

[9] Dawson and Dyson, *J. Chem. Soc.*, 1133 (1933).

[10] Long and Olson, *J. Phys. Chem.*, **41**, 267 (1937).

free of carboxyl groups, we find that their reactions fall into one or the other of two very definite groups. On the one hand the bimolecular substitution reactions, which we take to involve an inversion of configuration, have as their most constant characteristic a decrease in rate as the structure of the alkyl group is altered in the order methyl, ethyl, *s*-propyl, *t*-butyl. This retarding effect of the replacement of hydrogen by alkyl on the alpha carbon atom has been found in the reactions of alkyl halides with iodide ion,[11] with acetoacetate ion,[12] and with ethoxide,[13] phenoxide,[14] hydroxyl,[15] and thiosulfate[16] ions. It also appears in the reactions of alkyl halides with trimethylamine and with ammonia[17]

$$R_3N + RI \longrightarrow R_4N^+ + I^- \qquad (2)$$

Although the substituting group is unchanged the amine possesses the same unshared electron pair which is responsible for the reaction of the halide ion, the charge on the latter being a factor of subsidiary importance.

There are, on the other hand, a number of reactions of alkyl halides in which an exactly reverse order of reactivity is observed, the tertiary halides being most reactive and methyl least reactive. In this group are found the reactions with silver[18] and with mercuric salts.[19] It also includes, as Ingold and Hughes[20] have shown, a most interesting type of reaction which we shall call a *solvolysis*. Thus Ward[21] found that α-phenylethyl chloride, when dissolved in an alcohol–water mixture, liberates hydrochloric acid at a rate which is independent of the hydroxyl ion concentration of the solution. That is to say, the halide does not react directly with hydroxyl ion. The same effect, a first order solvolysis, is observed with other highly alkylated or phenylated alkyl halides, thus with benzhydryl chloride,[22] with *t*-butyl chloride,[23] and with triphenylmethyl chloride.[24] With methyl and ethyl halides the solvolysis is slower than the bimolecular substitution of hydroxyl for halide ion.[20] With halides of intermediate composition, *i*-propyl chloride,[25] *s*-butyl bromide,[26] and benzyl chloride,[27] the bimolecular substitution and the first order solvolysis have comparable rates.

There are, therefore, two competing reaction paths by which halide may be converted to alcohol which are of fundamentally different mechanism and of strikingly different dependence upon structure of reactant. If opposite signs of rotation, the typical phenomenon of the Walden inversion, are not found here, the probability of their ever appearing in the products of two one-step parallel reactions would seem to be extremely small. The available evidence obtained by Houssa, Kenyon and Phillips[28] is inconclusive because it requires for its interpretation the assumption that the reaction of lithium chloride with *s*-octyl toluenesulfonate involves an inversion of the configuration of the *s*-octyl group, an assumption which would only be justified were the necessary kinetic data available to determine whether the reaction is a bimolecular substitution of chloride ion for toluenesulfonate ion. We have therefore sought for independent and simpler evidence, and have found suitable material in the parallel reactions of an optically active halide with acetate ion on the one hand and with acetic acid on the other.

We have found that α-phenylethyl chloride reacts with tetraethylammonium acetate in acetone to form the corresponding phenylethyl acetate by a reaction whose kinetics show it unmistakably to be bimolecular. It is therefore a reaction of exactly the same type as that of iodide ion with alkyl chloride and it must be assumed to involve an inversion in configuration. On the other hand, the same chloride dissolved in glacial acetic acid reacts at a comparable rate to form the same product by a reaction which is just as unmistakably of the first order, the rate being independent of the concentration of acetate ion. An apparently favorable effect of alkali acetates upon the reaction turns out to result from the considerable reversibility of the reaction, the alkali acetate serving to advance the reaction only by suppressing the reverse process. These reactions are clearly parallel to the hy-

---

(11) Conant and Kirner, This Journal, **46**, 232 (1924).

(12) Wislicenus, *Ann.*, **212**, 239 (1882).

(13) Hecht, Conrad and Brückner, *Z. physik. Chem.*, **4**, 273 (1889).

(14) Segaller, *J. Chem. Soc.*, **103**, **1154**, **1421** (1913).

(15) De Bruyn and Steger, *Rec. trav. chim.*, **18**, 41, 311 (1899).

(16) Slator, *J. Chem. Soc.*, **85**, 1286 (1904); **87**, 482 (1905).

(17) (a) Menschutkin, *Z. physik. Chem.*, **5**, 589 (1890). (b) Preston and Jones, *J. Chem. Soc.*, **101**, 1930 (1912).

(18) Burke and Donnan, *ibid.*, **85**, 555 (1904).

(19) (a) Nicolet and Stevens, This Journal, **50**, 135 (1928); (b) Nicolet and Potts, *ibid.*, 212.

(20) Gleave, Hughes and Ingold, *J. Chem. Soc.*, 236 (1935).

(21) Ward, *J. Chem. Soc.*, 445 (1927).

(22) (a) Ward, *ibid.*, 2285 (1927); (b) Norris and Morton, This Journal, **50**, 1801 (1928).

(23) Hughes, *J. Chem. Soc.*, 255 (1935).

(24) Branch and Nixon, This Journal, **58**, 492 (1936).

(25) Hughes, *ibid.*, **57**, 708 (1935).

(26) French, McShan and Johler, *ibid.*, **56**, 1346 (1934).

(27) Olivier and Weber, *Rec. trav. chim.*, **53**, 869 (1934).

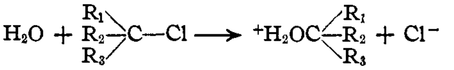
(28) Houssa, Kenyon and Phillips, *J. Chem. Soc.*, 1700 (1929).

droxyl ion and water reactions previously discussed. Nevertheless both reactions are found to lead to a phenylethyl acetate whose sign of rotation is opposite to that of the chloride used. That is to say, both reactions involve an identical change in configuration, and this as we have seen is assuredly an inversion. Our results in this most favorable case for the opposite hypothesis strongly support the thesis[2,4] that reactant and product in a substitution reaction will have identical configurations only when the reaction is a complex one involving an even number of simple substitution processes each of which inverts.

There is one important difference between the two reactions: very considerable racemization accompanies the solvolytic reaction in acetic acid, much less if any occurs in the bimolecular substitution in acetone. This difference seems indeed to be a rather frequent concomitant of the two reaction types, the bimolecular process showing little if any racemization in the extensive series of reactions studied by Kenyon and Phillips[2] and the solvolytic reaction giving rise sometimes but not always[29] to extensive loss in activity. Kenyon and Phillips[2] have attributed this racemization to the diversion of part of the reaction to a path which involves the intermediate appearance of an instantaneously racemizing carbonium ion. This is a possible but not a unique interpretation.

Several important conclusions about the relative configurations of compounds of this series follow. The hydrolysis of the halide to the alcohol is of exactly the same reaction type as the reaction with acetic acid, and consequently must involve an inversion. In agreement with this conclusion the levo-rotatory α-phenylethyl alcohol, which is obtained by hydrolysis from the dextro-rotatory chloride,[29a] may be esterified with acetic anhydride to the levo-rotatory acetate.[30] The latter, as we have shown, may also be formed by solvolysis in acetic acid from the same dextrorotatory chloride. Since the acetylation of the alcohol cannot conceivably alter the configuration of the α-carbon atom, the levo-alcohol and the levo-acetate must therefore have an identical configuration which is the enantiomorph of that possessed by the dextro chloride. The conclusion that hydrolysis inverts is also in agreement with the previously mentioned evidence of Houssa, Kenyon and Phillips.[28] The existing data also permit the conclusion that the conversion of α-phenylethyl alcohol to the chloride by hydrochloric acid or by phosphorus pentachloride involves an inversion, and that the conversion by thionyl chloride does not.[30] The principle that solvolytic reactions invert and that inversion also accompanies the reaction of alcohol with hydrogen chloride should be valid for all cases; the other reactions are so complex that no generalization is justified.

The conclusion that solvolytic reactions invert brings up most insistently the problem of the mechanism of this reaction type. The obvious explanation for the inversion would suppose that the reaction consists in a direct substitution of a solvent molecule for halide ion



$$H_2O + \begin{matrix}R_1\\R_2\\R_3\end{matrix}\!>\!C{-}Cl \longrightarrow {}^+H_2OC\!<\!\begin{matrix}R_1\\R_2\\R_3\end{matrix} + Cl^- \qquad (3)$$

followed or even accompanied by loss of hydrogen ion to form the carbinol. This reaction however is of exactly the same type as the reaction of an amine with an alkyl chloride, and there is every reason to suppose that it should show the same dependence upon structure.[17] The mechanism fails, therefore, to account for the most striking characteristic of the solvolytic reaction.

The failure is the more significant because the reason for the effect of these structural changes upon the reactivity seems to be perfectly clear in the case of all the other reactions. As Meer and Polanyi[31] have suggested, substitution of alkyl for hydrogen on the alpha carbon must increase the difficulty of bringing up the reacting ion or molecule on the side of that carbon atom opposite to the halide ion which is to separate, that is, on the side on which the alkyl groups project. This steric hindrance does not exist in the reactions with silver and mercuric salts in which the reaction mechanism involves the approach of the metallic ion to the halogen atom on the side away from the alkyl group.[32] An entirely different order of reactivity, which depends perhaps upon the effect of the substituent upon the strength of the carbon–halogen linkage therefore applies. The order of structural effects observed in the solvolytic reaction is consequently the one which applies in the case of those reactions in which the driving force derives from an attack upon halogen rather than upon carbon.

---

[29] (a) McKenzie and Clough, *J. Chem. Soc.*, **103**, 687 (1913); (b) Pickard and Kenyon, *Ber.*, **45**, 1592 (1912).

[30] Kenyon, Phillips and Taylor, *J. Chem. Soc.*, 173 (1933).

[31] Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

[32] Roberts and Hammett, THIS JOURNAL, **59**, 1063 (1937).

One might therefore conclude, as various investigators[20,22a,33] have done, that the reaction involves the intermediate formation of a carbonium ion, as it does in the reaction with mercuric salts,[32] except that such a conclusion seems completely inconsistent with our results on the configurational change. By all odds the most probable product of a reaction with a carbonium ion intermediate is a completely racemic one; but if any activity escaped it would be expected to depend upon the formation of a product with the original configuration.[2] The actual formation of active and inverted product definitely excludes the mechanism except for the racemic portion of the product. Even for this however there are difficulties. In the two cases in which a carbonium ion intermediate is most clearly indicated,[32,34] this exhibits the property of reacting to a considerable extent, even in the presence of a hydroxylic solvent, with negative ions, including those which are derived from strong acids, such as bromide or nitrate ion. In the present reaction such a property would lead to a reversible ionization of the alkyl halide and to a decrease in rate with increasing chloride ion concentration. Such a decrease has never been observed in a solvolytic reaction, and our experiments definitely prove its absence in the present case.

One arrives, therefore, at a reaction picture in which one or more molecules of hydroxylic solvent (water, alcohol or acetic acid) determine the reaction by virtue of their affinity for halide ion, while another molecule simultaneously lies in wait on the opposite side of the carbon–halogen linkage, ready to form the inverted reaction product. This picture is closely related to the one suggested by Ogg and Polanyi[35] of a solvation of the carbon–halogen dipole.

In view of the relatively high state of organization which exists in solvents of this type,[36] it is possible that still another solvent molecule simultaneously removes the proton. In any case the reaction is not bimolecular but *polymolecular*, the equation being

$$\mathrm{RCl} + n\,\mathrm{R'OH} \longrightarrow \mathrm{ROR'H^+} + \mathrm{Cl(R'OH)}_{n-1}^{-} \quad (4)$$

or

$$\mathrm{RCl} + n\,\mathrm{R'OH} \longrightarrow \mathrm{ROR'} + \mathrm{R'OH_2^+} + \mathrm{Cl(R'OH)}_{n-2}^{-} \quad (5)$$

Such a reaction must require the formation of a solvation complex of alkyl halide with solvent within which the necessary rearrangements leading to the reaction products occur.

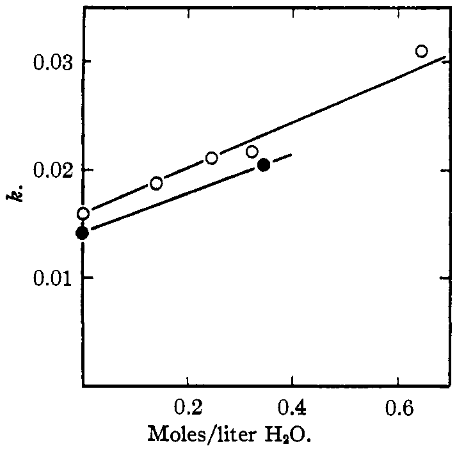


Fig. 1.—Effect of water on the rate of reaction: ○, experiments in the presence of lithium salts; ●, experiments in the presence of potassium salts.

The polymolecular nature of the solvolysis is strongly evidenced by the fact that it occurs only with a high concentration of hydroxylic molecules, that is, essentially only in a hydroxylic solvent. We have in this research dissolved α-phenylethyl chloride in a 1-molar solution of water in acetone, and allowed the mixture to stand for weeks without being able to observe a measurable reaction. At the same time the addition of water to an acetic acid solution of the halide produces a large and linear increase in the rate of solvolysis (see Fig. 1). If the solvolytic reactions were bimolecular this would mean the superimposition of a reaction with water upon the reaction with acetic acid. But such a reaction system would be inconsistent with the observed facts, first that the reaction in acetic acid containing water is still first order, and second that an even larger concentration of water in acetone gives rise to no measurable reaction. Further data in support of this argument will be presented in another paper from this Laboratory.[37]

Experimental

Materials.—Acetone was purified by the method of Conant and Kirner.[38] Acetic acid was refluxed with and then distilled from either chromic acid anhydride or phosphorus pentoxide. Immediately before use it was distilled from excess of triacetyl borate;[39] m. p. 16.52–16.60°,

---

(33) (a) Olivier and Berger, *Rec. trav. chim.*, **45**, 712 (1926).

(34) Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

(35) Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 619 (1935).

(36) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(37) Farinacci and Hammett, THIS JOURNAL, **59**, 2542 (1937).

(38) Conant and Kirner, *ibid.*, **46**, 232 (1924).

(39) La Mer and Eichelberger, *ibid.*, **55**, 3633 (1933).

corresponding to a maximum water content of 0.04%. Acetic anhydride was distilled in an all-glass still, retaining the middle third. Sodium acetate was recrystallized from water, and dried first at 40–50°, then at 125°; % $C_2H_3O_2$, found 72.0, calcd. 72.0.[40] It was used as primary standard for acid–base titrations in acetic acid. Potassium acetate was of reagent grade. Lithium acetate was dissolved in acetic acid and the resulting solution was filtered, refluxed with an equal volume of acetic anhydride, and evaporated to dryness *in vacuo*. The residue was dried at 125° and kept at that temperature; analysis (by titration with benzene sulfonic acid in acetic acid), formula weight, found 65.7, calcd. 66.0. Diphenylguanidine was recrystallized four times from toluene and once from benzene, and dried at 100°. Technical benzene sulfonic acid (a hydrate) was used for titrations.

Tetraethylammonium acetate was prepared from the C. P. bromide by treatment of the latter in aqueous solution with silver oxide, filtration, boiling till no odor of triethylamine was apparent, neutralization with acetic acid and evaporation under reduced pressure. The resultant pasty mass was dissolved in anhydrous acetone, and the solution cooled with solid carbon dioxide until no further crystals appeared. The mother liquid was decanted and the crystals were washed several times with anhydrous ether, and quickly transferred to a vacuum desiccator over phosphorus pentoxide. They soon turned into a heavy yellowish oil, which analyzed for $(C_2H_5)_4NC_2H_3O_2 \cdot H_2O$. Tetrabutylammonium acetate was prepared by the method of Fuoss, Cox and Kraus;[41] formula weight by titration in acetic acid, found 296, calcd. 301.

α-Phenylethyl alcohol was prepared by the reduction of acetophenone by sodium in ethyl alcohol, and purified by conversion to the acid phthalic ester, which was recrystallized twice from benzene. It was recovered from the ester by saponification with sodium hydroxide and steam distillation; b. p. 102–103° at 20 mm. α-Phenylethyl chloride was prepared by the action of hydrogen chloride in benzene or of thionyl chloride on the alcohol. It was washed with sodium carbonate solution, and with water, dried over sodium sulfate or calcium chloride and distilled; b. p. 78–79° at 15 mm. The final titers in the rate measurements in acetic acid indicated a purity of 95–98%; Volhard titrations or treatment with sodium ethoxide in ethyl alcohol gave 99% or better. Hydrolysis in alcohol–water mixtures without added base gave about 94%.[21]

Phenylethyl acetate was prepared by acetylation with acetic anhydride of the alcohol, followed by vacuum distillation; b. p. 103–104° at 16–17 mm. Calcd. C, 73.2; H, 7.3. Found: C, 72.99; H, 7.36.[42]

Kinetic Experiments in Acetic Acid.—The reaction of alkyl chloride with acetic acid at 50° was followed by back-titrating excess acetate ion in solution with a standard solution of benzenesulfonic acid in acetic acid, using crystal violet as the indicator.[43] Hydrogen chloride and benzenesulfonic acid act as strong acids in this medium, the alkali acetates as strong bases. Solutions were made up in a volumetric flask at 25° and 10-cc. portions were placed in sealed ampoules, the time of immersion in the 50° thermostat being taken as zero time for the rate measurements. The initial titer was obtained immediately on one portion; the end-titer was obtained on an ampoule which was kept in an oven at 125° for one and one-half to two days. For each experimental point an ampoule was chilled in ice, opened, rinsed out with anhydrous acetic acid, and titrated with 0.2 *m* benzenesulfonic acid measured from a weight buret. The reproducibility of the titration is shown by the data of Table I, obtained in the standardization of a benzenesulfonic acid solution against anhydrous sodium acetate.

TABLE I

NaOAc, g.	Acid solution, g.	Molality acid
0.1930	9.705	0.2423
.4161	20.911	.2426
.1673	8.459	.2411

When the alkyl chloride reacts with acetic acid in the absence of added acetate, an equilibrium is reached. This may be approached from both sides with consistent results as the data of Table II show. These were obtained by allowing the reaction to proceed for several days at 50°. K is the equilibrium constant $[RCl]/([ROAc][HCl])$.

TABLE II

Initial [RCl]	Initial [HCl]	Initial [ROAc]	Final [HCl]	K
0.1366	0	0	0.0248	182
.2654	0	0	.0355	181
0	0.0896	0.1028	.00833	178
0	.1126	.0862	.0356	234

In the presence of an ionized acetate, however, the acetate ion reacts with the hydrogen chloride, and the acetolysis proceeds to completion. The reaction follows a first order law in all cases. This is shown for three typical runs in Table III.

TABLE III

$[RCl] = 0.0880$ $[KOAc] = 0.198$			$[LiOAc]$ 0.104 $[RCl] = 0.0879$ $[LiCl] = 0.100$		
Time, hrs.	Titer	k	Time, hrs.	Titer	k
0	8.872	....	0	4.641	....
18.2	7.969	0.0142	17.3	3.692	0.0159
35.4	7.268	.0150	28.1	3.279	.0151
59.6	6.609	.0142	42.3	2.701	.0160
85.6	6.086	.0142	65.0	2.083	.0161
107.3	5.779	.0142	88.6	1.642	.0162
139.5	5.552	.0131	137.4	1.044	.0174
∞	4.918	....	∞	0.702	....
$[RCl]$ 0.0848; $[LiOAc]$ 0.109; $[LiCl]$ 0.100; $[H_2O]$ 0.382					
0	4.489	....	60.8	1.916	0.0186
13.1	3.520	0.0224	85.4	1.231	.0227
24.6	2.920	.0216	113.1	0.933	.0242
39.1	2.264	.0225	∞	.687	....

The results of all the experiments are summarized in Table IV. The average deviation of the values within a run, which included always from four to six points, varied from 0.0002 to 0.0006 except in the case of two experiments, nos. 16 and 17, in which the high concentration of

---

[40] Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1928, Vol. II, p. 157.

[41] Fuoss, Cox and Kraus, *Trans. Faraday Soc.*, **31**, 749 (1935).

[42] Microanalysis by S. Gottlieb.

[43] Nadeau and Branchen, THIS JOURNAL, **57**, 1363 (1935).

TABLE IV

No.	[RCl]	Acetate		Other solutes				k
1	0.0846	Li	0.196					0.0117
2	.1600	Li	.199					.0115
3	.0844	Li	.0962	LiCl	0.100			.0162
4	.0856	Li	.0966	LiCl	.100			.0164
5	.0879	Li	.104	LiCl	.100			.0162
6	.0965	Li	.148	LiCl	.050			.0128
7	.0863	Li	.0491	LiCl	.150			.0174
8	.0908	DPG[a]	.194					.0195
9	.0735	DPG[a]	.0941	DPG[a]Cl	.100			.0198
10	.0880	K	.198					.0142
11	.0885	TBA[b]	.203					.0225
12	.0845	Li	.0970	LiCl	.100	AA[c]	0.0690	.0150
13	.0790	Li	.0971	LiCl	.100	AA[c]	.1807	.0143
14	.0800	Li	.0975	LiCl	.100	H_2O	.1407	.0187
15	.0810	Li	.0970	LiCl	.100	H_2O	.244	.0212
16	.0848	Li	.109	LiCl	.100	H_2O	.323	.0218
17	.0850	Li	.0999	LiCl	.100	H_2O	.645	.0309
18	.0880	K	.198	H_2O	.342			.0205

[a] DPG diphenylguanidinium. [b] TBA tetrabutylammonium. [c] AA acetic anhydride.

water had an adverse effect upon the precision of the titration. In no case was a drift in the constants perceptible. The reaction is seen to be first order in alkyl halide (expts. 1 and 2), and of excellent reproducibility (expts. 3 to 5). The constant varies somewhat with changing concentration of lithium acetate, even though the ionic strength is maintained constant by the addition of lithium chloride (expts. 1, 5, 6, and 7) but this effect does not appear when the cation is diphenylguanidinium ion (expts. 8 and 9). Further the rate is different in the presence of the same concentration of different acetates (expts. 1, 8, 10, and 11). These effects are obviously of the nature of specific salt effects, whose appearance is not surprising in a solvent with so low a dielectric constant, and they do not in the slightest impugn the conclusion that the reaction is of the first order. Acetic anhydride has a small retarding effect (expts. 3, 12 and 13), and water has a pronounced accelerating action (expts. 3, 10, and 14 to 18). The water effect is linear, as Fig. 1 demonstrates. Chlorides do not retard (expts. 1 to 7).

Experiments in Acetone.—These were likewise carried out at 50°. The procedure of making up solutions in acetone of tetraethylammonium acetate and α-phenylethyl chloride and distribution in 10-cc. portions in sealed ampoules was as much as in the experiments in acetic acid. For analysis the contents of the ampoule were rinsed with two 5-cc. portions of acetone and two similar portions of water into a separatory funnel containing 100 cc. of water and 100 cc. of benzene. The water layer was separated, boiled to remove benzene and acetone, and titrated with silver nitrate solution with chromate indicator. Blank experiments showed that the extraction procedure does not appreciably hydrolyze the alkyl chloride. The reaction is somewhat complicated by the fact that the tetraethylammonium chloride crystallizes out in the course of the reaction.

Table V reports detailed data on two typical experiments, the titer being given in cc. of 0.123 molar silver nitrate. Both first order and second order constants are listed as k_1 and k_2, respectively. In Table VI the constants for six runs are tabulated, the first four being based upon data of the same sort as those exhibited in Table V, the last two depending on measurements made only after the reaction was well over 50% complete.

TABLE V

$[(Et)_4NOAc] = 0.531$				$[(Et)_4NOAc] = 0.0988$			
$[RCl] = 0.1706$				$[RCl] = 0.0562$			
Time, hrs.	Titer	k_1	k_2	Time, hrs.	Titer	k_1	k_2
2.25	2.01	0.0702	1.77	1.82	1.29	0.183	2.03
4.23	2.77	.0524	1.65	3.80	2.08	.160	1.90
6.25	3.28	.0438	1.57	5.82	2.61	.143	1.83
8.63	3.58	.0344	1.45	8.20	2.97	.128	1.65
Av. of k_2 1.60 ± 0.09				Av. of k_2 1.85 ± 0.11			

TABLE VI

	$[(Et)_4NOAc]$	[RCl]	k_1	k_2
1	0.0531	0.1706	0.0502 ± 0.012	1.60 ± 0.09
2	.0988	.0562	.154 ± .02	1.85 ± .11
3	.0569	.0652	.0802 ± .015	1.90 ± .11
4	.1183	.1260	.145 ± .025	1.69 ± .11
5	.0433	.0516	.0407 ± .003	1.61 ± .04
6	.0923	.0519	.0989 ± .004	1.61 ± .03

These data demonstrate beyond all question that the reaction is of the second order. It is clearly not of the first order, and the minor deviations from the second order law which do appear are of the magnitude to be expected of salt effects or other results of changing medium, and may indeed result solely from the relatively large experimental error of the analytical determination.

Experiments on Optically Active Materials.—α-Phenylethyl alcohol was resolved by the method of Houssa and Kenyon,[44] the product having a specific rotation of +41.93°. This highly active material was diluted with inactive carbinol before use. The active α-phenylethyl chloride was prepared by slow addition of the active carbinol to 3 or 4 times its weight of freshly distilled thionyl chloride, addition of an equal volume of chloroform, ex-

---

[44] Houssa and Kenyon, *J. Chem. Soc.*, 2260 (1930).

traction with sodium carbonate solution and water, drying, removal of the solvent, and distillation under reduced pressure: b. p. 79–80° at 16 mm.; Cl, found by Volhard titration 24.8, 25.2%, calculated 25.2%.

Optical measurements were made in a 10-cm. polariscope tube immersed in a thermostat at 25.00°. The polariscope was a Schmidt and Haensch instrument which could be read to 0.01°. Readings were taken to the nearest 0.1°. The source of illumination was a mercury arc lamp; the Hg green line (wave length 5461) was used.

The following experiments were performed: (1) 12.55 g. of α-phenylethyl chloride ($\alpha = +8.50°$, obtained from a sample of alcohol with $\alpha = +9.7°$) and 9.81 g. of anhydrous potassium acetate dissolved in anhydrous acetic acid to make a total volume of 500 cc. were kept at 50° for one week. The solution was decanted from the potassium chloride, the acetic acid was removed under reduced pressure, and the residue was poured into water, extracted with benzene, and dried over calcium chloride. After removal of the solvent, the product was distilled under reduced pressure. The portion which distilled below 101° at 15 mm. was rejected in addition to several cc. of the acetate ester. The remainder distilled at 104° at 17 mm. and showed no test for chloride. It showed the following analysis: C, 73.21%; H, 7.3%.[42] Calculated for phenylethyl acetate C, 73.2%; H, 7.3%. The specific rotation was −1.1°, being opposite in sign to the original alcohol, and considerably racemized.

(2) Fourteen grams of alkyl halide ($\alpha = +6.0°$) and 19 g. of tetraethylammonium acetate dissolved in anhydrous acetone to make a volume of 500 cc. were kept for four days at 50°. The acetone was distilled off and the residue worked up as in (1). Seven and two-tenths grams of phenylethyl acetate boiling at 97° at 12 mm. was obtained with the analysis C, 73.5%; H, 7.6%.[42] It gave a slight test for chloride. The specific rotation was −4.7°, of the same sign as that obtained in (1) but much less racemized.

(3) A solution of 10 g. of alkyl chloride ($\alpha = +13.7°$) dissolved in 300 cc. of anhydrous acetone, was allowed to stand for two months. Thereupon 15 g. of tetraethylammonium acetate was added, and the solution was allowed to stand at room temperature for several weeks. On working up as before 7 g. of phenylethyl acetate boiling at 105–107° at 17 mm. was obtained. The specific rotation was −11.5°. Clearly then the halide does not racemize spontaneously in acetone solution. It is most improbable therefore that it ionizes to form carbonium and chloride ions in this medium at an appreciable rate.

The extensive investigations of Hughes, Ingold and coworkers[45] on Reaction Kinetics and the Walden Inversion had not become available at the time when this article was submitted for publication. There is no essential contradiction between their conclusions, based upon different material, and our own.

Summary

The solvolytic reaction of α-phenylethyl chloride in anhydrous acetic acid at 50° has been shown to be essentially of the first order. The reaction of the same chloride with tetraethylammonium acetate in acetone at the same temperature has been shown to be of the second order. Both reactions produce a levo-rotatory phenylethyl acetate from dextro-rotatory chloride, racemization being greater in the first case. In the light of this and other data it is shown that the first order solvolytic reactions of alkyl halides in water, alcohol, and acetic acid are most probably of a polymolecular nature, involving several molecules of the solvent, and that the driving force derives largely from the energy of solvation of the halide ion.

[45] Hughes, Ingold, *et al.*, *J. Chem. Soc.*, 1196, 1201, 1208, 1236, 1243, 1252 (1937).

NEW YORK, N. Y. RECEIVED JULY 13, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Polymolecular Solvolytic Reactions: Water Catalysis in the Alcoholysis of Benzhydryl Chloride[1]

BY NICHOLAS T. FARINACCI AND LOUIS P. HAMMETT

The first order reactions of solvolysis which alkyl halides undergo with solvents of the nature of water, alcohol or acetic acid[2] offer a reaction mechanism problem of the first importance. We have approached this by a method which starts from the observation of Norris and Morton[3] that the first order constant (independent of the acidity or alkalinity of the solution) for the formation of hydrogen chloride in a solution of benzhydryl chloride in ethyl alcohol is subject to a large increase upon the addition of water. As Fig. 1 shows, this increase is linear in the water concentration within the range of what may properly be called dilute solutions of water in alcohol. A

---

[1] Thesis submitted by Nicholas T. Farinacci in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] (a) Ward, *J. Chem. Soc.*, 445 (1927); (b) Ward, *ibid.*, 2285 (1927); (c) Hughes, Ingold and Shapiro, *ibid.*, 225 (1936); (d) Steigman and Hammett, THIS JOURNAL, 59, 2536 (1937); (e) Nicolet and Stevens, *ibid.*, 50, 135 (1928).

[3] Norris and Morton, *ibid.*, 50, 1795 (1928).