

Intermediates Common to the Reactions of
Hydrochlorination of Styrene and Ionization of
1-Phenylethyl Chloride¹

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Electrophilic addition, nucleophilic substitution, and elimination have long been considered to proceed by similar carbonium intermediates and a considerable amount of definite information regarding the energetics of the various steps in a particular system can be obtained by approaching it from different directions under very similar conditions. These reactions have been tied together in an elegant study reported by Noyce on a system which involves dissociated ions.² Thus, the acid-catalyzed hydration-dehydration reactions of the stilbenes are described in great detail where the energy differences for the various ground states and transition states are provided quantitatively. On the other hand, the intermediates invoked in the chlorination³ and hydrochlorination^{4,5a,6a} of olefins in weakly dissociating solvents are ion pairs similar to those produced in solvolysis reactions.^{7,8} We felt that it was important to investigate in a similar way a system that involves ion pairs. The phenylethyl-styrene system in acetic acid is particularly attractive since it can be compared to the solvolysis of phenylethyl chloride (RCl), which has been extensively studied in the more nucleophilic aqueous solvents,^{5b,6b,d,9,10} and more directly with the data on the hydrochlorination of styrene in AcOH which is available at various temperatures.^{4c} We now wish to communicate the results of a comparative study on this system.

Solvolysis of 1-phenylethyl chloride in anhydrous acetic acid containing 0.01 M lithium acetate at 75.0° produces 86% 1-phenylethyl acetate and 14% styrene. The rate of acetolysis followed by analysis of inorganic chloride ion¹¹ provides a value for k_t equal to $3.8 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$ at low lithium acetate concentrations. The k_t values listed in Table I show a slight increase by added lithium acetate, where the "b" value is *ca.* 0.5. Optically active 1-phenylethyl chloride was prepared from the resolved carbinol¹² with thionyl chloride.¹³ The loss of optical activity which accompanies the acetolysis reaction of RCl was measured in an all-glass cell thermostated at 75.0°. The rate of loss of optical activity proceeds substantially faster than acetolysis where the value of k_α is equal to $10.0 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$. The final reaction solutions were >98.5% racemic.¹⁴ The racemization rate constant, k_{rac} , provided by the difference between k_α and k_t , is equal to $6.17 \times 10^{-5} \text{ sec}^{-1}$. Thus, the k_{rac}/k_t ratio of 1.6 indicates that the ionization reaction must proceed *via* ion-pair intermediates which racemize and return to covalent RCl *ca.* 1.6 times faster than they go on to products.

In order to test the intramolecular nature of the racemization process, the rates of chlorine exchange k_e were measured between RCl and radiolabeled lithium chloride. The pseudo-first-order k_e values at 0.013–0.035 M LiCl are small compared to the overall reaction and at an average $[\text{Cl}^-]$ of 0.02 M, chlorine exchange is less than 6% of the total return reaction ($k_e/k_{rac} = 0.06$). Therefore, the return does not occur from dissociated intermediates to any great extent.^{7c}

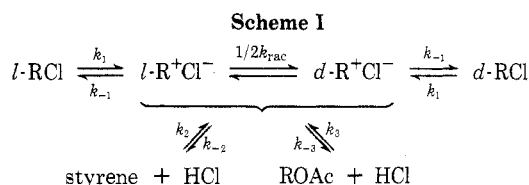
The partitioning of the intermediates to produce covalent RCl and ROAc as based on these measurements differs widely from the hydrochlorination of styrene. The hydrochlorination of styrene^{4c} in AcOH containing 0.01 M HCl produces a kinetic product mixture containing 93%

Table I
Summary of k 's for 1-Phenylethyl
Chloride^a in Acetic Acid at 75.0°

Salt	$10^5 k, \text{sec}^{-1}$		
	k_α	k_t	k_e
0.0569 M LiOAc	10.06 ± 0.3		
0.0569 M LiOAc	9.92 ± 0.3		
0.0103 M LiOAc		3.81 ± 0.23	
0.0257 M LiOAc		3.84 ± 0.10	
0.0569 M LiOAc		3.88 ± 0.15	
0.0103 M LiOAc			0.26 ± 0.03
0.0130 M LiCl			
0.0128 M LiOAc		3.9	0.46 ± 0.08
0.0288 M LiCl			
0.0103 M LiOAc			0.58 ± 0.08
0.0346 M LiCl			

^a RCl concentrations are 0.01 M for k_t and k_e measurements and 0.07 M for k_α measurements.

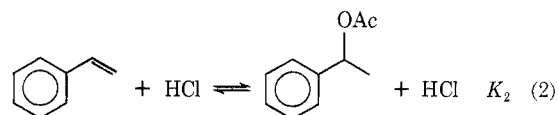
RCl plus 7% ROAc at 25° and 85% RCl plus 15% ROAc at 75°. Thus the RCl/ROAc formation ratio is 5.6 from the addition reaction and 1.86 from the ionization reaction. In Scheme I is presented a simple mechanistic scheme, with a minimum number of required intermediates, which will fit the results from the two reactions. This scheme is



based on the assumption that the two reactions produce the same ion-pair intermediates and that the discrepancy in the results is due to the lack of an adequate measure of k_1 .

Given the scheme, the k_{-1}/k_{-3} ratio estimated equal to 5.6 from the RCl/ROAc product ratio produced in the hydrochlorination reaction and the k for formation of ROAc equal to $3.3 \times 10^{-5} \text{ sec}^{-1}$ provide a better measure of k_1 equal to $18.5 \times 10^{-5} \text{ sec}^{-1}$ ($\Delta F^* = 26.30 \text{ kcal}$). Therefore, total return occurs >98% *via* intimate ion pairs.

The partitioning of the intermediate is such that it returns to RCl (85%) and produces ROAc (15%), providing a $\Delta\Delta F^*$ difference for these processes equal to 1.19 kcal. Of the return reaction, only 33% proceeds with racemization; *i.e.*, the rate of inversion is more endothermic than return by 1.24 kcal. From the ratio of the kinetic products in the acetolysis of RCl one calculates 1.25 kcal as the energy difference for the transition states leading to these products. Finally in order to provide all the energetics corresponding to Scheme I, one could use K_1 equal to *ca.* 180⁹ for eq 1 where $\Delta\Delta F_{eq}$ is equal to 3.58 kcal at unit concentrations, and the value of k for the reaction of styrene with 1 M HCl in AcOH at 75° of $1.21 \times 10^{-3} \text{ sec}^{-1}$,^{4c,15} with ΔF^* equal to 25.10 kcal. These energy values are plotted in Figure 1. By difference, the energy associated with the equilibrium in eq 2 provides a value of K_2 equal to one in AcOH at 75°.



Regarding the nature of the transition states for the formation of products, based on the deuterium isotope effects in the solvolysis of RCl, this particular transition

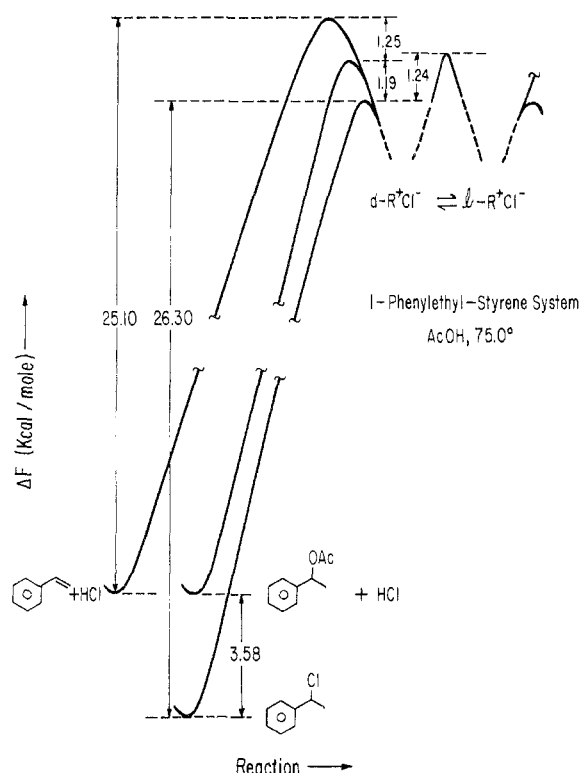


Figure 1.

state must look very much like the intermediate with little covalent bonding of the cation to chloride ion or solvent.^{6a}

Considering the nature of the ion-pair intermediates produced in the solvolysis reactions of compounds which produce open carbonium ions, when the counterion is a benzoate⁸ or an arylsulfonate⁷ anion, racemization does not occur at the "intimate" ion pair but instead occurs exclusively and efficiently at the "solvent-separated" ion pair. Chemical capture also occurs at this intermediate. However in the solvolysis of the corresponding alkyl halides, racemization and chemical capture is not restricted to the more loose ion pair, but instead racemization can occur at the intimate ion pair stage.^{7,16,17} Thus the present results can be fit by the presence of one intimate ion pair common to both reactions which can return to RCl and can racemize. The extent of racemization that accompanies the solvolysis reaction depends on the sensitive balance between the nucleophilicity and dissociating power of the solvent. Because of the difficulty in estimating these properties of solvents, caution must be used in attempting to combine quantitatively those results obtained in different solvents or solvent mixtures with varying per cent composition.

An alternative explanation for greater formation of RCl in the hydrochlorination reaction relative to solvolysis is the possible presence of a concurrent concerted addition pathway which yields RCl exclusively. The decrease in the RCl/ROAc product ratio from 13 to 6 as the solvent changes to the higher ionizing solvent, CF₃CH₂OH,^{4a,c} is consistent with this possibility.

Experimental Section

Optically active 1-phenylethyl alcohol was prepared by the method of McKensie and Clough where the 1-phenylethyl acid phthalate brucine salt was recrystallized several times from anhydrous acetone. The carbinol was converted to the alkyl chloride with thionyl chloride. The reaction mixture was dissolved in pentane and the solution was washed carefully with aqueous NaHCO₃. The solution was then dried over K₂CO₃ and the pen-

tane was removed under reduced pressure. The alkyl chloride was used as such without further purification, [α]_D²⁰ -38.8°, chloride analysis 99.9% Cl.

The purification of acetic acid solvent and preparation of the salt solutions used in the experiments were performed as previously described.¹¹ The polarimetric rate measurements were made in a thermostated 1-dm all-glass cell using a Perkin-Elmer polarimeter, Model 141. The titrimetric rate measurements were carried out in sealed ampoules.¹¹ The k_{α} and k_t values were calculated using the integrated first-order rate expression.

The exchange rate measurements were carried out using a sealed-ampoule technique as previously described.¹¹ The separation of organic chloride from inorganic chloride was afforded using pentane and water. Aliquots (2 ml) from each layer were delivered into 10 ml of Bray's solution¹⁸ and the radioactivity level was measured using a Beckman LS100 liquid scintillation counter. The pseudo-first-order exchange rate constants, k_e , were calculated using a modified form of the equation of Swart and Roux¹⁹

$$k_{et} = \frac{2.303[\text{LiCl}]}{([\text{RCl}] + [\text{LiCl}])} \log \left[1 - \gamma e^{k_{et}t} \frac{([\text{RCl}] + [\text{LiCl}])}{[\text{RCl}]} \right]$$

where γ is the fraction of the radioactivity found in the pentane layer.

Product analysis were performed as previously described.¹¹

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Registry No.—1-Phenylethyl chloride, 672-65-1.

References and Notes

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