

the routes leading to dehydrohalogenation and to exchange ($k_1^D + k_1^E$).

The slope of the plot k_α vs. $[\text{Et}_4\text{NCl}]$ is linear and is twice the slope of the plot k_E vs. $[\text{Et}_4\text{NCl}]$ leading to $k_2^\alpha = 2k_2^E$. This signifies that each act of bimolecular radiochlorine exchange proceeds with inversion of configuration and suggests that k_2^E is the rate constant for SN2 attack by chloride ion on covalent 1-phenylethyl chloride.⁶

The kinetics of substitution of *p*-methylbenzhydryl chloride by $\text{Y} = \text{Cl}^-$, N_3^- , pyridine, and triethylamine in nitromethane follow eq. 1, containing concurrent first- and second-order terms. The kinetics of the

$$V = k[\text{RCI}] = k_1[\text{RCI}] + k_2[\text{RCI}][\text{Y}] \dots \quad (1)$$

first-order component, $k_1[\text{RCI}]$ (Table I), embody three features: (a) the initial rates of substitution are practically the same: $k_1^{\text{Cl}^-} = k_1^{\text{N}_3^-} = k_1^{\text{pyr}} = k_1^{\text{NEt}_3}$; (b) the ionic strength effects are similar and positive; and (c) in the nonsymmetric substitutions by N_3^- , pyridine, and NEt_3 , added Et_4NCl (common ion) is able to depress the entire first-order component leaving the second-order component largely unchanged. This behavior is analogous to the one found for benzhydryl bromide in nitromethane,⁷ and more recently for *p*-chlorobenzhydryl chloride by Diaz and Winstein.⁵

TABLE I

VALUES OF k_1^E , $k_1^{\text{N}_3^-}$, k_1^{pyr} , $k_1^{\text{NEt}_3}$, AND k_1^α (IN SEC.^{-1}) AT A NUMBER OF TEMPERATURES

Temp., °C.	$10^6 k_1^E$	$10^6 k_1^{\text{N}_3^-}$	$10^6 k_1^{\text{pyr}}$	$10^6 k_1^{\text{NEt}_3}$	$10^6 k_1^\alpha$
0.0	0.019	0.021	0.020	0.020	0.54 ^a
25.0	0.474	0.46	0.47	0.45	
25.7					8.9 ^a
34.8	0.95			0.93	
35.6					19.0 ^a
44.6	2.26	2.25	2.20	2.28	47.0 ^a
60.0	10.0	10.0	9.6		

^a Hydrogen chloride exerts a powerful effect on k_1^α . Pyridine was added to eliminate catalysis by hydrogen chloride. Similar results were obtained when HCl was rendered inert by adding tribenzyl amine or Et_4NCl .

The kinetics of racemization of *p*-methylbenzhydryl chloride⁸ in the presence of $[\text{Et}_4\text{NCl}^{36}] < 0.043 M$ or [pyridine] $< 0.056 M$ follow eq. 2.⁹

$$V_\alpha = k_\alpha[\text{RCI}] = k_1^\alpha[\text{RCI}] \dots \quad (2)$$

The Arrhenius equation for the component of unimolecular radiochlorine exchange is: $\log k_1^E = 8.2 - 18,600/(2.3RT)$ while that for racemization is: $\log k_1^\alpha = 8.6 - 17,300/(2.3RT)$. The ratio of k_1^α/k_1^E decreases with increase in temperature.

(6) E. D. Hughes, F. Juliusberger, A. D. Scott, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1173 (1936).

(7) Y. Pocker, *ibid.*, 3939, 3944 (1959).

(8) Details of the resolution of *p*-methylbenzhydryl and its conversion to optically active chloride are in the Ph.D. thesis of William A. Mueller, University College, University of London, Sept., 1959.

(9) At temperatures below 50° and $[\text{NEt}_4\text{Cl}] < 0.043 M$ the bimolecular components, $k_2^E[\text{RCI}][\text{Et}_4\text{NCl}^{36}]$ and $k_2^\alpha[\text{RCI}][\text{Et}_4\text{NCl}]$, are very small. They become significant at higher $[\text{Et}_4\text{NCl}]$. Values of k_1^E and k_1^α for 60.0° were obtained by extrapolation to $[\text{Et}_4\text{NCl}] = 0$.

We interpret k_1^E as the rate of dissociation of *p*-methylbenzhydryl chloride. However, k_1^α is much larger than k_1^E and we associate the former with ion pair return,^{4,5} after reorganization.

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The Hydrogen Chloride Catalyzed Radiochlorine Exchange and Racemization of Aralkyl Chlorides in Nitromethane^{1,2}

Sir:

In polar nonsolvolytic media the stoichiometric composition of the activated complex is clearly defined, the possible structures of the transition state are more easily scrutinized, and short-lived intermediates interact reversibly with solvent molecules.³ The ionizing solvent nitromethane, although not entirely inert toward carbonium ions,⁴ is sufficiently unreactive toward aralkyl halides to permit a study of the mechanism of electrophilic catalysis by molecular HCl.

The kinetics of racemization of 1-phenylethyl chloride in the presence of HCl in nitromethane follow eq. 1. At 99.8°, $k_1^\alpha = 1.2 \times 10^{-5} \text{ sec.}^{-1}$ and $k_2 = 1.5 \times$

$$V_\alpha = k_\alpha[\text{RCI}] = k_1^\alpha[\text{RCI}] + k_2^\alpha[\text{RCI}][\text{HCl}] \dots \quad (1)$$

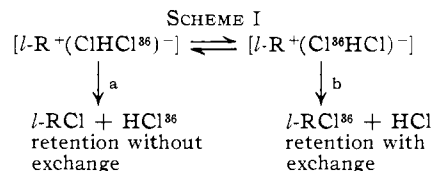
$10^{-3} \text{ l. sec.}^{-1}$.

Isotopic chlorine exchange between 1-phenylethyl chloride and hydrogen radiochloride was studied over a reagent concentration, $[\text{HCl}] = 0.03\text{--}0.11 M$, in nitromethane. The stoichiometric reaction in this region is one of substitution because $d[\text{olefin}]/dt = 0$; the first-order rate coefficients, k_E , increase linearly with the concentration of HCl (eq. 2). At 99.8°,

$$V_E = k_E[\text{RCI}] = k_1^E[\text{RCI}] + k_2^E[\text{RCI}][\text{HCl}^{36}] \dots \quad (2)$$

$k_1^E = 0.29 \times 10^{-5} \text{ sec.}^{-1}$ and $k_2^E = 1.52 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$.

The value of k_1^E is practically the same as that obtained for dehydrohalogenation⁵ in the presence of



(1) This work was supported in part by a grant from the National Science Foundation.

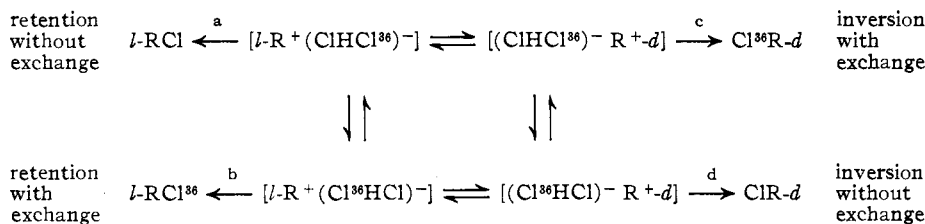
(2) Presented in part at the Nineteenth IUPAC Congress, London, 1963.

(3) Y. Pocker, "Nucleophilic Substitution at a Saturated Carbon Atom in Nonhydroxylic Solvents," in "Progress in Reaction Kinetics," Pergamon Press, Vol. 1, 1961, pp. 218, 227, 228.

(4) H. Burton and G. W. H. Cheesman, *J. Chem. Soc.*, 832 (1953); Y. Pocker, *ibid.*, 240 (1958).

(5) Y. Pocker, W. A. Mueller, F. Naso, and G. Tocchi, *J. Am. Chem. Soc.*, **86**, 5011 (1964).

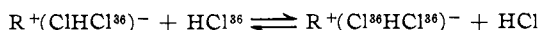
SCHEME II



pyridine and NEt_4Cl acting as bases: $k_1^D = 0.29 \times 10^{-5}$ sec^{-1} . This indicates that whatever the stoichiometry of these unimolecular processes, substitution or elimination, the rates are controlled by a common process which is identified as the rate of production of chemically capturable 1-phenylethyl cations, this rate being slower than the racemization process.

The component of exchange which is first order in alkyl chloride and first order in HCl cannot be an SN_2 process, because $k_2^\alpha = k_2^E$. It appears that, in contrast to $\text{NEt}_4\text{Cl}^{36}$,⁵ the HCl^{36} molecule is intervening in the rate-controlling step of the second-order process by virtue of its capacity to form a hydrogen bond with the chlorine of 1-phenylethyl chloride, and thus assists electron transfer and bond heterolysis.⁶ The intermediates involved in k_2^E cannot be *tight* ion pairs because the collapse of $\text{R}^+(\text{ClHCl}^{36})^-$ if occurring on the same side of R^+ would lead to $k_2^E > k_2^\alpha$. This can be seen from Scheme I. Even if we were to allow for rapid reorganization of the ion pair in the solvent cage prior to collapse as indicated in Scheme II, we would find that statistically two routes lead to inversion (c and d) and two routes lead to exchange (b and c). Such a mechanism would lead to $k_2^\alpha = 2k_2^E$.

The experimentally found equality between k_2^α and k_2^E requires for kinetic reasons that the equilibration of radiochlorine between bichloride ion and the HCl^{36} in solution



be faster than the recombination (collapse) of the carbonium ion with one of the chlorines of the hydrogen bichloride ion. This isotopic equilibration can be achieved either if the ion pairs in question are long lived to allow time for diffusion through the solvent cage or if both k_2^E and k_2^α represent the rate constants for the formation of kinetically free R^+ and $(\text{ClHCl}^{36})^-$.

The rates of racemization and exchange of *p*-methylbenzhydryl chloride in nitromethane increase linearly with $[\text{HCl}^{36}] < 0.11 M$. At 44.6° , V_α and V_E follow eq. 1 and 2, respectively, with $k_1^\alpha \cong 48 \times 10^{-5} \text{sec}^{-1}$; $k_1^E \cong 2.28 \times 10^{-5} \text{sec}^{-1}$; and $k_2^\alpha = k_2^E = 0.47 \text{l. mole}^{-1} \text{sec}^{-1}$. We take the ratio $k_2^\alpha/k_2^E = 1.0$ to mean that the energy barriers for HCl^{36} catalyzed racemization and exchange are the same and that consequently they measure a common process, *e.g.*, the formation of loosely associated or possibly dissociated species of the type $\text{R}^+ + (\text{ClHCl}^{36})^-$ or $(\text{CH}_3-$

(6) Molecular hydrogen chloride is a recognized electrophilic catalyst for such ionic processes as the rearrangement of camphene hydrochloride in nitrobenzene [P. D. Bartlett and I. Pöckel, *J. Am. Chem. Soc.*, **60**, 1585 (1938); Y. Pocker, *Proc. Chem. Soc.*, 216 (1960)] and for the ionization of *t*-butyl chloride in nitromethane [Y. Pocker, *J. Chem. Soc.*, 1972 (1960)].

(7) A kinetically free $(\text{ClHCl}^{36})^-$ would rapidly equilibrate its chlorines with those of HCl^{36} .

$\text{NO}_2\text{R})^+ + (\text{ClHCl}^{36})^-$,⁸ in which the $(\text{ClHCl}^{36})^-$ group rapidly exchanges chloride with other labeled HCl^{36} molecules.

(8) It is interesting to compare these observations with those reported for HgCl_2 assisted ionization of *p*-chlorobenzhydryl chloride in acetone [A. Ledwith, M. Hojo, and S. Winstein, *Proc. Chem. Soc.*, 241 (1961)].

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Primary and Secondary Solvent Isotope Effects

Sir:

We wish to describe the quantitative separation and evaluation of the primary and secondary solvent isotope effects on the acid cleavage of allylmercuric iodide. In aqueous solutions containing 10^{-4} – $10^{-5} M$ substrate, an equimolar amount of sodium iodide, and 10^{-3} – $10^{-1} M$ perchloric acid, 1 mole of propene (measured manometrically and identified mass spectroscopically) and 1 mole of mercuric iodide (identified and measured by its ultraviolet spectrum) are produced from each mole of starting material. When crotylmercuric iodide is used as the substrate, 95% of the gaseous product is 1-butene. (The other 5% is *cis*-2-butene.)

The rate, measured by following the disappearance of the substrate ultraviolet spectrum, is accurately first order in substrate to >95% of completion, and the usual integrated form of the first-order rate law¹ was used to evaluate pseudo-first-order rate constants, k_1 . In 10^{-3} to $10^{-1} M$ perchloric acid solutions $k_1/(\text{H}^+)$ is constant apart from a small electrolyte effect. The infinite dilution value of $k_1/(\text{H}^+)$, k_H , is $4.0 \pm 0.1 \times 10^{-2} \text{l. mole}^{-1} \text{sec}^{-1}$ at 35° .² Although iodide ion is catalytic, it increases $k_1/(\text{H}^+)$ by <5% at $10^{-4} M$.

In solutions containing methyl-di(β -cyanoethyl)amine and its perchloric acid salt in a fixed ratio, with the ionic strength held constant by added sodium perchlorate, k_1 showed a linear dependence on the buffer concentration, implying general acid catalysis.

A value of $1.23 \pm 0.06 \times 10^{-2} \text{l. mole}^{-1} \text{sec}^{-1}$ was obtained for k_D , by the same means used to determine k_H but with 99.7% D_2O as solvent. The greater fractional uncertainty may be due to the sensitivity of the derived k_D to contamination of the solvent with atmospheric moisture. This leads to a value of 3.25 for k_H/k_D .

These facts show, beyond reasonable doubt, that the rate-determining step is proton transfer to the γ -carbon

(1) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 27–31.

(2) This value is the average of ten determinations, corrected for the electrolyte effect. The uncertainty is the average deviation from the mean.