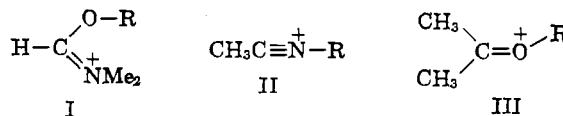solvents. Further, in $MeNO_2$, MeCN, and Me_2CO, the k_{2e} values for p-chlorobenzhydryl chloride are either nearly identical with or somewhat larger than those for the unsubstituted benzhydryl chloride. The available evidence suggests that the k_{2e} values are rate constants for SN2 attack[2c] on covalent RCl. A similar conclusion has been reached by Pocker[5] in the case of bromide exchange of benzhydryl bromide in $MeNO_2$.

The $k_e{}^0$ intercept values represent rate constants for formation of capturable intermediates extrapolated to zero salt concentration. In $MeNO_2$, MeCN, and DMF, the $k_e{}^0$ values are smaller than those for benzhydryl chloride by factors of 2.4–2.5, so that the p-Cl substituent effect is in line with the idea that $k_e{}^0$ is associated with ionization of RCl. For benzhydryl bromide in $MeNO_2$, Pocker[5] observed the same intercept values from bromide exchange or reaction with triethylamine, and he also noted common ion depression of the amine reaction by bromide salt. On this basis, he concluded that the capturable intermediate is the dissociated carbonium ion. Analogously, the capturable intermediate for the $k_e{}^0$ values in all four aprotic solvents may well be a dissociated species.[6]

In Table II are summarized $k_\alpha{}^0/k_t{}^0$ ratios for the solvolyzing solvents and $k_\alpha{}^0/k_e{}^0$ ratios for the aprotic ones. These values are lower limits for the ratio of

TABLE II

RATE COMPARISONS FOR RCl AT 75.0°

Solvent	D	$k_\alpha{}^0/k_e{}^0$	$k_\alpha{}^0/k_t{}^0$
AcOH (25°)	6		38
80% Me_2CO (25°)	30		2.6
$MeNO_2$	37	44	
MeCN	37	304	
$HCONMe_2$	37	4	
Me_2CO	21	>50	

ionization rate to rate of chemical capture.[2] They are also lower limits to the ratio of rate of ionization to rate of formation of dissociated carbonium ions.[2] Very interesting is the large range of $k_\alpha{}^0/k_e{}^0$ values in the aprotic solvents. Most striking are the values in $MeNO_2$, MeCN, and DMF, three solvents with essentially identical dielectric constants. In DMF the ratio is as low as 4, while in CH_3CN it is as high as 304. The most plausible single factor responsible for the large solvent specificity of the $k_\alpha{}^0/k_e{}^0$ ratios in these three solvents is nucleophilic solvent intervention which makes $k_e{}^0$ a larger fraction of $k_\alpha{}^0$ than it would otherwise be. For example, in the case of DMF, cation I would be an intermediate for the $k_e{}^0$ rate. Such solvent intervention is conceivable with the other aprotic solvents as well, salts of the I, II, and III types being known.[7] The present data suggest that

(5) Y. Pocker, *J. Chem. Soc.*, 3939, 3944 (1959).

(6) With p-chlorobenzhydryl chloride and triethylamine in $MeNO_2$ at 75°, the situation is quite complex. First-order rate constants for the amine reaction, followed by amine consumption or chloride ion formation, obey an equation like (1) with the intercept the same as for chloride exchange. Further, in the presence of sufficient Et_3N, the exchange reaction with Bu_4NCl has its intercept $k_e{}^0$ value suppressed to *ca.* zero and its k_{2e} slope is relatively unaffected. The product of the amine reaction is not the RN$^+$-Et_3Cl^- salt, however. The latter, independently prepared, decomposes rapidly at 75° with chloride ion disappearance, and subsequently chloride ion slowly reappears.

(7) H. Meerwein, *et al.*, *Angew. Chem.*, **67**, 374 (1955); *Ber.*, **89**, 209, 2060 (1956).

the tendency for such nucleophilic solvent intervention is high for DMF[8] and low for CH_3CN.

$$H-C\underset{\overset{+}{N}Me_2}{\overset{O-R}{\diagdown}} \qquad CH_3C\equiv\overset{+}{N}-R \qquad \underset{CH_3}{\overset{CH_3}{\diagdown}}C=\overset{+}{O}{\diagup}R$$
$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$

While an ion like I would be sufficiently long-lived to become a dissociated cation (free of the counter chloride ion), the nucleophilic intervention of DMF in the radiochloride exchange scheme must occur at a stage of ionization–dissociation of RCl earlier than the dissociated R$^+$ ion. If DMF attacks a carbonium chloride ion pair, one can understand $k_e{}^0$ being sensitive to solvent nucleophilicity, while $k_\alpha{}^0$ is not.

(8) See, *e.g.*, F. C. Chang and R. T. Blickenstoff, *J. Am. Chem. Soc.*, **80**, 2906 (1960), for nucleophilic attack by DMF; for related effects of $MeNO_2$ and Me_2CO, see Y. Pocker, *J. Chem. Soc.*, 240 (1958); H. Burton and G. W. H. Cheeseman, *ibid.*, 832 (1953); R. A. Sneen and H. Weiner, *J. Am. Chem. Soc.*, **85**, 2181 (1963).

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Radiochlorine Exchange and Racemization of 1-Phenylethyl Chloride and p-Methylbenzhydryl Chloride in Nitromethane[1,2]

Sir:

In the presence of added pyridine, the initial first-order rate coefficients of styrene, acid, and chloride ion production from 1-phenylethyl chloride at 99.8° in solvent nitromethane are practically identical (*i.e.*, dehydrohalogenation) and independent of pyridine concentration: $V_D = k_1{}^D[RCl]$ with $k_1{}^D = 0.29 \times 10^{-5}$ sec.$^{-1}$. In the presence of added Et_4NCl^{36}, $V_D = k_1{}^D[RCl] + k_2{}^D[RCl][Et_4NCl]$ with $k_1{}^D = 0.29 \times 10^{-5}$ sec.$^{-1}$ and $k_2{}^D \simeq 2.0 \times 10^{-5}$ sec.$^{-1}$ l. mole^{-1}, but the radiochlorine exchange[3] is a strictly bimolecular process: $V_E = k_E[RCl] = k_2{}^E[RCl][Et_4NCl^{36}]$, with $k_2{}^E = 6.1 \times 10^{-3}$ sec.$^{-1}$ l. mole^{-1}. For racemization we find $V_\alpha = k_\alpha[RCl] = k_1{}^\alpha[RCl] + k_2{}^\alpha[RCl][Et_4NCl^{36}]$, where $k_1{}^\alpha = 1.2 \times 10^{-5}$ sec.$^{-1}$ and $k_2{}^\alpha = 12.4 \times 10^{-3}$ sec.$^{-1}$ l. mole^{-1}. It will be noticed that in the unimolecular region, $[NEt_4Cl] \to 0$, the polarimetric rate coefficient, $k_1{}^\alpha$, for the formation of racemic starting material and product is about four times larger than the rate coefficient for chemical capture, $(k_1{}^D + k_1{}^E) \simeq k_1{}^D$.[4] The route corresponding to $k_1{}^\alpha$ is associated with ion pair return after reorganization[4,5]; its free energy of activation is lower than that 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) The rate of loss of tracer from Et_4NCl^{36} contains a term due to the dehydrohalogenation of 1-phenylethyl chloride (isotopic dilution) and a term due to substitution (isotopic exchange). To obtain the true component of isotopic exchange we corrected for dehydrohalogenation. The values thus obtained have also been confirmed by determining the rate of incorporation of Cl^{36} into 1-phenylethyl chloride.

(4) In liquid SO_2, $k_1{}^\alpha/(k_1{}^D + k_1{}^E) \simeq 9$: Y. Pocker, *Trans. Faraday Soc.*, **55**, 1266 (1959); *cf.* also Y. Pocker, "Nucleophilic Substitution at a Saturated Carbon Atom in Nonhydroxylic Solvents," Vol. 1, Pergamon Press, New York, N. Y., 1961, pp. 227, 228.

(5) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, **No. 22**, 12 (1960); S. Winstein, A. Ledwith, and M. Hojo, *ibid.*, **No. 10**, 341 (1961); A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **86**, 5010 (1964).

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

The slope of the plot k_α vs. [Et$_4$NCl] is linear and is twice the slope of the plot k_E vs. [Et$_4$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 Y = Cl$^-$, N$_3^-$, pyridine, and triethylamine in nitromethane follow eq. 1, containing concurrent first- and second-order terms. The kinetics of the

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

first-order component, $k_1[\text{RCl}]$ (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$_4$NCl (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.	$10^5 k_1^E$	$10^5 k_1^{\text{N}_3^-}$	$10^5 k_1^{\text{pyr}}$	$10^5 k_1^{\text{NEt}_3}$	$10^5 k_1^\alpha$
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$_4$NCl.

The kinetics of racemization of p-methylbenzhydryl chloride[8] in the presence of [Et$_4$NCl^{36}] < 0.043 M or [pyridine] < 0.056 M follow eq. 2.[9]

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

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^α = 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-methylbenzhydrol 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 [NEt$_4$Cl] < 0.043 the bimolecular components, k_2^E[RCl][Et$_4$NCl^{36}] and k_2^α[RCl][Et$_4$NCl], are very small. They become significant at higher [Et$_4$NCl]. Values of k_1^E and k_1^α for 60.0° were obtained by extrapolation to [Et$_4$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^α = 1.2 × 10^{-5} sec.$^{-1}$ and k_2 = 1.5 ×

$$V_\alpha = k_\alpha[\text{RCl}] = k_1^\alpha[\text{RCl}] + k_2^\alpha[\text{RCl}][\text{HCl}] \quad \dots \quad (1)$$
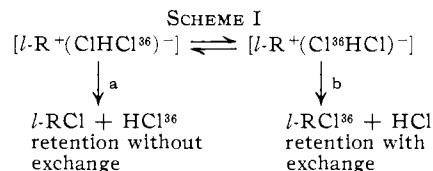
10^{-3} l. sec.$^{-1}$.

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

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

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

The value of k_1^E is practically the same as that obtained for dehydrohalogenation[5] in the presence of

SCHEME I

$$[l\text{-R}^+(\text{ClHCl}^{36})^-] \rightleftharpoons [l\text{-R}^+(\text{Cl}^{36}\text{HCl})^-]$$

   ↓ a   ↓ b

l-RCl + HCl^{36} l-RCl^{36} + HCl
retention without   retention with
exchange   exchange

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(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).