vergent than are those of polyethylene and polydimethylsiloxane.[39]

# Kinetics of the Exchange of Chlorine Atoms between Hydrogen Chloride and Benzyl Chlorides. Solvent Effects[1,2]

Warren Bruce, Milton Kahn, and Joseph A. Leary

*Contribution from the University of New Mexico, Albuquerque, New Mexico, and the University of California Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Received February 8, 1965*

*The rate of exchange of chlorine atoms between hydrogen chloride and p-nitrobenzyl chloride in 82% dioxane–18% water by weight solution is represented by the rate law: $R_e = 2.04 \times 10^{11} e^{-22,600/RT} \alpha(HCl)(PNBC) + 2.76 \times 10^8 e^{-19,600/RT}(1 - \alpha)(HCl)(PNBC)$, where $\alpha$ is the degree of dissociation of the hydrogen chloride and $R_e$ is the rate of exchange in mole $l.^{-1} sec.^{-1}$. The reaction mechanism is believed to be an example of a bimolecular process in which both the chloride ion and the hydrogen chloride ion pair participate. Ordinary fluorescent light has no detectable effect on the rate of exchange, and the over-all rate of exchange is decreased by added lithium perchlorate. Analytical expressions were developed which allow for the hydrolysis of the organic halide during the exchange. No exchange was detected between hydrogen chloride and p-nitrobenzyl chloride in anhydrous benzene after 363 hr. at 60.00°. Similarly, no exchange was observed with benzyl chloride in benzene and acetone. The exchange with benzyl chloride proceeds at a faster rate in ethanol than in dioxane. In dioxane, p-nitrobenzyl chloride exchanges at a larger rate than benzyl chloride.*

## Introduction

The work presented here is primarily concerned with the exchange of chlorine atoms between hydrogen chloride and *p*-nitrobenzyl chloride in 82% dioxane–18% water by weight solutions. This system is of particular interest since the thermodynamic data for hydrogen chloride in dioxane–water mixtures have been extensively investigated[3]; furthermore, this system affords an opportunity to study an exchange in a medium of low dielectric constant and relatively high solvating power.

The mechanism of certain nucleophilic substitution reactions has been the subject of some controversy; *i.e.*, some reactions are considered to take place either *via* a single intermediate mechanism having both unimolecular (SN1) and bimolecular (SN2) properties or by concurrent unimolecular and bimolecular processes. Bird, Hughes, and Ingold[4] have proposed a theory in support of the idea that the mechanisms merge into each other, and the interpretation by Bensley and Kohnstam[5] of the solvolysis of benzyl chloride in 50% by volume aqueous acetone lends support to this point of view. Gold[6] criticized this argument on the theoretical ground that the postulation of fractional reaction orders is incompatible with the current formulation of the laws of thermodynamics. Hill and Fry[7] have studied chlorine isotope effects in the reactions of substituted benzyl chlorides with cyanide and thiosulfate ions in 80% dioxane–20% water by weight solutions and concluded that there is a smooth transition in the reaction mechanism from SN1 to SN2 as the electron-donating power of the substituent increases. Pocker[8] takes the position that there is scope for both concurrent as well as intermediate SN1–SN2 mechanisms, the concurrent mechanisms being predominant in nonsolvolytic media where very short-lived intermediates cannot be irreversibly captured by a solvent molecule in the solvation cage. Casapieri and Swart[9] have reported that the exchange of radioactive chloride between diphenylmethyl chloride and lithium chloride in dimethylformamide is an unambiguous example of concurrent first- and second-order nucleophilic substitution.

Arguments exist in the literature to substantiate the position that ion pairs are not effective as nucleophilic reagents; on the other hand, compelling evidence has been presented to show that both ions and ion pairs are reactive. The second-order rate coefficient for the exchange between lithium radiochloride and benzyl chloride in dimethylformamide decreased as the concentration of the salt increased; however, Casapieri and Swart[9] have shown that a constant value is obtained on the assumption that only the chloride ion is reactive.

(1) This paper is a portion of the dissertation presented by W. Bruce in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June 1962; presented before the Physical Chemistry Division, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

(2) Under Contract W-7405-Eng-36 with the U. S. Atomic Energy Commission.

(3) (a) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 11; (b) B. B. Owen and G. W. Waters, *J. Am. Chem. Soc.*, 60, 2371 (1938); (c) F. Hovarka, R. A. Schaefer, and D. Dreisbach, *ibid.*, 58, 2264 (1936).

(4) M. L. Bird, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 634 (1954).

(5) B. Bensley and G. Kohnstam, *ibid.*, 4747 (1957).

(6) V. Gold, *ibid.*, 4633 (1956).

(7) J. W. Hill and A. Fry, *J. Am. Chem. Soc.*, 84, 2763 (1962).

(8) Y. Pocker, *Progr. Reaction Kinetics*, 1, 218 (1961).

(9) P. Casapieri and E. R. Swart, *J. Chem. Soc.*, 4342 (1961).

Winstein, et al.,[10] have pointed out that the apparent nucleophilic order, LiI > LiBr > LiCl, can be reversed if the second-order rate coefficients are divided by the respective degree of dissociation of the salts, the order then being in accord with that observed for tetra-*n*-butylammonium halides: $Bu_4NCl > Bu_4NBr > Bu_4NI$. Lichtin and Rao[11] found that both ions and ion pairs are involved in the exchange between *p*-nitrobenzyl bromide and a series of bromides in liquid sulfur dioxide. Ross, Finkelstein, and Petersen[12] have interpreted the rates of reaction of benzyldimethylanilinium ion and thiocyanate ion in four solvents from the standpoint of ion-association equilibria and specific rates for associated and nonassociated reactions. Bowers and Sturtevant[13] concluded that the exchange between *p*-nitrobenzyl bromide and lithium bromide in acetone–methanol–water took place primarily through the ion. The exchange reaction described here appears to be an example of a bimolecular process involving both the chloride ion and the hydrogen chloride ion pair.

## Experimental

*Radioactivity.* The 4.4 × 10⁵-year chlorine-36, which was used as the tracer, was obtained from the Oak Ridge National Laboratory as a 1.92 $M$ hydrochloric acid solution of 99% radiochemical purity with a specific activity of 520 $\mu$c./g. of chlorine. The activity of a standard sample prepared from this solution showed no change after 14 months.

*Chemicals.* Eastman White Label *p*-nitrobenzyl chloride (PNBC) was recrystallized twice from ethanol, dried, and stored over calcium chloride in a vacuum desiccator that was wrapped in aluminum foil.

J. T. Baker Chemical Co. analytical grade benzyl chloride was dried with calcium chloride for 24 hr., and then distilled at 17 mm.; the middle portion of the distillate, which boiled in the range of 70.5 to 71.5° (17 mm.), was retained.

J. T. Baker Chemical Co. analytical grade benzene was refluxed with molten potassium for 48 hr. under a stream of dry argon, stored over potassium under a dry argon atmosphere, and distilled from the metal immediately before use.

Fisher Chemical Co. purified grade *p*-dioxane was further purified by the method of Hess and Frahm[14] and stored under a dry argon atmosphere, in the dark, no longer than 48 hr. The 82% dioxane–18% water by weight solutions were prepared by weighing 90 ± 0.01 g. of water into 410 ± 0.01 g. of dioxane; these mixtures were used immediately after preparation.

J. T. Baker Chemical Co. C.P. grade acetone was dried 48 hr. with colorless Drierite and then distilled under argon in the dark, the middle fraction being retained for use.

Gray Chemical Co. dispersed sodium, containing 50% sodium metal by weight in mineral oil, was used without purification. The dispersed sodium was tested for and found to be free of chloride.

Lithium perchlorate, prepared from Mallinckrodt perchloric acid and lithium carbonate, was recrystallized five times from water.

The mercurous nitrate solution was 0.01 $f$ in nitric acid and contained 16.9 g./l. of $HgNO_3 \cdot H_2O$; free mercury was added to the reagent to prevent oxidation to mercury(II).

Demineralized water was distilled from alkaline permanganate and stored in a polyethylene bottle.

All other chemicals were of reagent grade and were used without further purification.

*Preparation of Dioxane–Water Reaction Mixtures.* A weighed quantity of *p*-nitrobenzyl chloride was placed in a 200-ml. flask and dissolved in 50 ml. of solvent which was 82% dioxane and 18% water by weight. A measured volume of aqueous radioactive hydrogen chloride of known concentration was added with a micropipet. The amount of water added in the hydrochloric acid solution was calculated from the density–composition data on hydrochloric acid,[15] and a measured volume of anhydrous dioxane was added to adjust the solvent composition to 82% dioxane by weight. The solution was made up to the mark with a final portion of the dioxane–water solvent. The concentration of the *p*-nitrobenzyl chloride was determined by both alkalimetry and argentimetry. A portion (20 ml.) of the reaction mixture was placed in a 50-ml. erlenmeyer flask and titrated to the phenolphthalein end point with standard sodium hydroxide. A blank titration was run on a portion of the dioxane–water solvent. The titrations were carried out under a blanket or argon to improve the sharpness of the end point. Another portion of the reaction mixture was titrated according to the modified Volhard method.[16] The two analytical procedures agreed with ±0.3%. The faster alkalimetric technique was used in most cases. It was found that the *p*-nitrobenzyl chloride did not interfere with either the alkalimetric or argentimetric methods. In four of the runs a measured volume of 3.88 $M$ lithium perchlorate was added. The amount of water added by this procedure was calculated from the density–composition data on aqueous lithium perchlorate,[17] and a measured volume of anhydrous dioxane was added to adjust the solvent composition to 82% dioxane by weight.

*Preparation of Anhydrous Solvent Reaction Mixtures.* Radioactive hydrogen chloride, generated *in vacuo* (10⁻⁵ mm.) from the reaction between dry radioactive potassium chloride and sulfuric acid, was passed through two 250-mm. Pyrex traps cooled with acetone–Dry Ice mixtures, and condensed in a receiver containing the anhydrous solvent which was frozen with liquid nitrogen. The receiver was brought to room temperature, filled with dry argon, and removed from the vacuum line. The hydrogen chloride solution was transferred to a 250-ml. volumetric flask containing a weighed amount of the organic halide and diluted to the mark with the desired solvent.

(10) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, **9**, 24 (1960).
(11) N. N. Lichtin and K. N. Rao, *J. Am. Chem. Soc.*, **83**, 2417 (1961).
(12) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **83**, 4853 (1961).
(13) S. D. Bowers, Jr., and J. M. Sturtevant, *ibid.*, **77**, 4903 (1955).
(14) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, pp. 284, 285.
(15) C. D. Hodgman, R. C. Weast, and C. W. Wallace, "Handbook of Chemistry and Physics," 35th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953, p. 1837.
(16) J. R. Caldwell and H. V. Mayer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 38 (1935).
(17) T. W. Newton and F. B. Baker, unpublished data, Los Alamos Scientific Laboratory, Los Alamos, N. M.

*Procedure for Making the Exchange Runs and Separating the Reactants.* Aliquots (20 ml.) of the reaction mixture were added to the reaction vessels from a 50-ml. buret which was equipped with a Teflon needle valve and a 15-cm. long capillary tip. Light was excluded from the reaction mixture by wrapping the vessels with aluminum foil. The Pyrex vessels consisted of a 20-ml. bulb fitted with a 14.0-cm. long, 9-mm. o.d. X 5-mm. i.d. glass tube. After the vessels had been filled with the desired reaction mixture, they were cooled in an ice–water bath and sealed with a torch. When the vessels were placed in the thermostat, the solution expanded and the residual vapor volume was less than 0.5% of the total volume. Thermal equilibrium was considered to be attained when the solution expanded to the end of the stem of the reaction vessel, which generally took about 3 min. The temperature of the thermostat was regulated to ±0.02° and was measured with a Beckmann thermometer which had been calibrated to ±0.01° against a platinum-resistance thermometer by the Los Alamos standards laboratory group. After thermal equilibrium was attained, the first sample was removed from the thermostat and plunged into a salt–ice–water bath and the time noted. Approximately 1 min. was required for the solution to contract to its volume at 20°. Zero time for the exchange was reckoned from the time the first sample was removed from the thermostat. Time was measured by an electric wall clock which had a sweep second hand. The end of the stem of the reaction vessel was broken off by applying a hot glass rod, and the contents of the reaction vessel was washed into a glass-stoppered 50-ml. centrifuge tube which contained benzene and water. The bottom of the tube had been drawn to a point to facilitate separation of the phases. The mixture was shaken for 1 min. and centrifuged for 3 min. in a clinical centrifuge. The aqueous layer was drawn off with a capillary pipet and the benzene layer washed with 3 ml. of distilled water. The benzene layer was then tested for chloride ion by washing with water and testing the washings with silver nitrate solution. The washings showed no turbidity after standing for 24 hr. The washed benzene, which contained the organic halide, was retained for subsequent treatment with dispersed sodium. The two aqueous portions were combined and washed with 5 ml. of benzene. The benzene from this last step was discarded, and the aqueous phase, containing the hydrogen chloride, was retained for use in the precipitation step.

*Counting Technique.* Solid samples of mercurous chloride, prepared according to methods described elsewhere,[18] were counted with a methane-flow proportional counter operating at atmospheric pressure and 4200 v. The specific activity of each sample was corrected for the variation in counting rate with sample thickness. The coincidence correction and error due to statistical fluctuations in counting rate were each less than 1%.

*Determination of the Specific Activities of the Hydrogen Chloride and Organic Chloride Fractions.* The specific activities of the hydrogen chloride and organic chloride fractions were measured in counts per minute per milligram of mercurous chloride as described under

"Counting Techniques." Aliquots of the aqueous hydrogen chloride solutions were taken such that the weights of the mercurous chloride precipitates would be approximately the same for a given run; aliquots of benzene solutions of the benzyl chlorides were similarly taken. The aliquot of organic halide in benzene was transferred to a 50-ml. centrifuge tube, and sufficient benzene was added to make the total volume approximately 10 ml. The solution was treated with 10 drops of 2-propanol and 1 ml. of dispersed sodium.[19] The resulting reaction proceeded for 5 min. after which the excess sodium was allowed to react with methyl alcohol. Distilled water (10 ml.) was added and the solution neutralized to the phenolphthalein end point with nitric acid. After neutralization, the solution was centrifuged and the aqueous layer removed with a capillary pipet and filtered through a Whatman No. 41H filter paper. The chloride was then precipitated with mercurous nitrate solution.

## Calculations

The logarithmic form of the isotopic exponential exchange law governing a simple, homogenous, isotopic exchange reaction between HCl and an organic chloride, RCl, is

$$R_e t = -\frac{(\text{HCl})(\text{RCl})}{(\text{HCl}) + (\text{RCl})} \ln(1 - F) \qquad (1)$$

where $R_e$ is the constant rate of exchange of chlorine atoms between HCl and RCl in gram-atoms per liter per unit time, $t$ is the time, (HCl) and (RCl) are the molar concentrations of HCl and RCl, respectively, and $F$ is the fraction exchange.[20] At a given temperature the rate law for the reaction can be determined by relating $R_e$ and the concentration of the reactants; thus, a concurrent first- and second-order exchange, involving ions and ion pairs, can be described by

$$R_e = k_1(\text{RCl}) + ki\alpha(\text{HCl})(\text{RCl}) +$$
$$km(1 - \alpha)(\text{HCl})(\text{RCl}) \qquad (2)$$

where $k_1$, $ki$, and $km$ are specific rate constants, and $\alpha$ is the degree of dissociation of the inorganic halide.

For the exchange studies in aqueous dioxane, it was necessary to consider the hydrolysis of the organic chloride. Assuming the hydrolysis to be irreversible[21] and a rate law given by eq. 2, it can be shown (see Appendix) that the fraction exchange, $F_{\text{RCl}}$, observed in RCl, varies with time as

$$\ln(1 - F_{\text{RCl}}) = -k_1 t - \frac{k_1}{k_H} \times$$
$$\ln \frac{[(\text{HCl})^0 + (\text{RCl})^0 - (\text{RCl})^0 e^{-k_H t}]}{(\text{HCl})^0} -$$
$$[(\text{HCl})^0 + (\text{RCl})^0]kt \qquad (3)$$

where $(\text{HCl})^0$ and $(\text{RCl})^0$ are initial molar concentrations of HCl and RCl, respectively, $k_H$ is the hydrolysis constant for the first-order hydrolysis of RCl, and $k$ is the summation $ki\alpha + km(1 - \alpha)$. For an exchange where $k_H t$ is small, eq. 3 assumes the following form

(18) M. Kahn, A. J. Freedman, R. D. Feltham, and N. L. Lark, *Nucleonics*, 13, 58 (1955).

(19) R. L. Menville and W. W. Parker, *Anal. Chem.*, 31, 1901 (1959).
(20) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 9.
(21) (a) G. W. Beste and L. P. Hammett, *J. Am. Chem. Soc.*, 62, 248 (1940); (b) J. W. Hackett and H. C. Thomas, *ibid.*, 72, 4962 (1950).

$$\ln(1 - F_{RCl}) = -\frac{[(HCl)^0 + (RCl)^0]}{(HCl)^0}k_1t -$$

$$[(HCl)^0 + (RCl)^0]kt \quad (4)$$

which shows that plots of $\ln(1 - F_{RCl})$ against time should be linear, in which case the effect of hydrolysis can be neglected. Where no hydrolysis occurs eq. 4 follows directly from eq. 1 and 2. As pointed out by Luehr, Challenger, and Masters,[22] if the reaction is second order, the hydrolysis of RCl has no effect on the plot of $\ln(1 - F_{RCl})$ vs. time. Thus, with $k_1 = 0$, eq. 3 yields directly

$$\ln(1 - F_{RCl}) = [(HCl)^0 + (RCl)^0]kt \quad (5)$$

If hydrolysis takes place then, regardless of the mechanism for exchange, the fraction exchange, $F_{HCl}$, observed in the HCl fraction will not agree with the fraction exchange, $F_{RCl}$, observed in the RCl fraction. The expression

$$[1 - F_{HCl}]\frac{(RCl)^0[(HCl)^0 + \Delta(HCl)]}{(HCl)^0[(RCl)^0 - \Delta(HCl)]} = [1 - F_{RCl}] \quad (6)$$

where $\Delta(HCl)$ is the change in the concentration of HCl during the exchange reaction, relates $F_{HCl}$ and $F_{RCl}$ (see Appendix).

Values of the dissociation constant, $K$, and the average distance of closest approach, $a$, for hydrogen chloride in 82% dioxane–18% water by weight solutions at 15, 25, 35, and 45° are tabulated by Harned and Owen.[3a] For the present work values of $K$ were required at 50.27 and 60.00°. These values were obtained by extrapolation of the linear plot of $K$ vs. $(DT)^3/Q_B$ where $D$ is the dielectric constant of the solvent and $Q_B$ is taken from the Bjerrum equation as described in Harned and Owen.[23] For these higher temperatures, $D$ was calculated employing the equation given by Harned and Owen,[24] and $a$ was obtained by extrapolation of the linear plot of this quantity against temperature.

Values of the mean ionic molal activity coefficient, $\gamma_\pm$, for hydrogen chloride, over the temperature range 5 to 45° and over the molal concentration range 0.001 to 0.500, have been tabulated.[25] Values of $\gamma_\pm$ at 50.27 and 60.00° were extrapolated with the aid of values of the relative partial molal heat content, $\bar{L}_2$, for hydrogen chloride. The parameters $\alpha$ and $\beta$ for the equation

$$\bar{L}_2 = \alpha + \beta T^2 \quad (7)$$

over the temperature range 0 to 50°, have been tabulated.[26] The dependence of $\gamma_\pm$ on temperature can be derived from the relation

$$\left[\frac{\delta(\ln a_2)}{\delta T}\right]_{P,m} = -\frac{\bar{L}_2}{RT^2} \quad (8)$$

where $a_2$ is the activity of the hydrogen chloride and $m$ is the molality. Substitution of $(m\gamma_\pm)^2$ for $a_2$ followed by integration leads to

(22) C. P. Luehr, G. E. Challenger, and B. J. Masters, *J. Am. Chem. Soc.*, **78**, 1314 (1956).
(23) Reference 3a, p. 72.
(24) Reference 3a, p. 162.
(25) Reference 3a, p. 718.
(26) Reference 3a p. 722.

$$\ln\frac{(\gamma_\pm)_T}{(\gamma_\pm)_{298}} = -\frac{\alpha}{2R}\left[\frac{T - 298}{298T}\right] - \frac{\beta}{2R}[T - 298] \quad (9)$$

For the purposes of the present investigation, the slight difference between the mean molal activity coefficient and the mean molar activity coefficient was neglected.

The degree of dissociation, $\alpha$, of hydrogen chloride was calculated from the equation

$$\alpha = 1 - \frac{C(\gamma_\pm)^2}{K} \quad (10)$$

where $C$ is the molar concentration of the hydrogen chloride.

The concentrations of the reactants were corrected for the expansion of the solvents with temperature by applying the appropriate densities of dioxane–water,[3c] benzene,[27] and acetone.[28]

## Results of Exchange Experiments with *p*-Nitrobenzyl Chloride in 82% Dioxane–18% Water Solution

The results of the exchange experiments in dioxane-water are summarized in Table I. The plots of log

Table I. Results of Exchange Runs with *p*-Nitrobenzyl Chloride in 82% Dioxane–18% Water by Weight Solutions

| Temp., °C. | (HCl),[a] M | (PNBC),[a] M | Half-time, hr. | $R_e/$ (PNBC) $\times 10^8$,[b] sec.$^{-1}$ | $R_e/\alpha \cdot$ (HCl)$\cdot$ (PNBC) $\times 10^8$,[b] l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|
| 24.91 | 0.0102 | 0.0499 | 1180.0 | 2.78 | 0.69 |
| 45.00 | 0.00121 | 0.0487 | 115.5 | 4.05 | 6.83 |
| 45.00 | 0.00246 | 0.0975 | 66.5 | 7.11 | 7.13 |
| 45.00 | 0.00490 | 0.0976 | 74.5 | 12.36 | 7.58 |
| 45.00 | 0.00733 | 0.0976 | 76.2 | 17.63 | 8.09 |
| 50.27 | 0.00121 | 0.0485 | 72.1 | 6.36 | 10.80 |
| 50.27 | 0.00250 | 0.0971 | 43.5 | 11.13 | 10.39 |
| 50.27 | 0.00488 | 0.0971 | 45.0 | 20.42 | 11.31 |
| 50.27 | 0.00738 | 0.0970 | 48.3 | 28.05 | 11.28 |
| 50.27 | 0.0123 | 0.0484 | 87.0 | 44.70 | 11.59 |
| 50.27 | 0.0124 | 0.1460 | 33.0 | 45.60 | 11.86 |
| 50.27 | 0.0125 | 0.0974 | 49.0 | 45.60 | 11.86 |
| 50.27 | 0.0194 | 0.0484 | 83.4 | 66.10 | 12.68 |
| 50.27 | 0.0244 | 0.0484 | 79.8 | 80.70 | 12.80 |
| 50.27 | 0.0247 | 0.0971 | 49.9 | 78.10 | 12.50 |
| 50.27 | 0.0482 | 0.1460 | 33.4 | 143.10 | 14.00 |
| 50.27 | 0.0485 | 0.0194 | 94.5 | 145.20 | 14.40 |
| 50.27[c] | 0.00490 | 0.0971 | 50.2 | ... | ... |
| 50.27[d] | 0.00490 | 0.0971 | 54.4 | ... | ... |
| 50.27[e] | 0.00492 | 0.0970 | 56.9 | ... | ... |
| 50.27[f] | 0.00491 | 0.0971 | 58.1 | ... | ... |
| 60.00 | 0.00121 | 0.0479 | 29.1 | 16.29 | 33.20 |
| 60.00 | 0.00242 | 0.0960 | 16.6 | 28.45 | 36.10 |
| 60.00 | 0.00483 | 0.0960 | 18.3 | 50.40 | 38.70 |
| 60.00 | 0.00724 | 0.0961 | 18.8 | 71.60 | 37.80 |

[a] (HCl) and (PNBC) are the molar concentrations of hydrogen chloride and *p*-nitrobenzyl chloride corrected for expansion of the solvent. [b] $R_e$ is the rate of exchange and $\alpha$ is the degree of dissociation of the hydrogen chloride. [c] 0.00471 $M$ in LiClO₄. [d] 0.00941 $M$ in LiClO₄. [e] 0.0141 $M$ in LiClO₄. [f] 0.0188 $M$ in LiClO₄.

$(1 - F_{PNBC})$ against time are linear and demonstrate that, in accordance with eq. 3 and 4, the hydrolysis of the organic halide can be neglected.

(27) "International Critical Tables of Numerical Data. Physics Chemistry, and Technology," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 29.
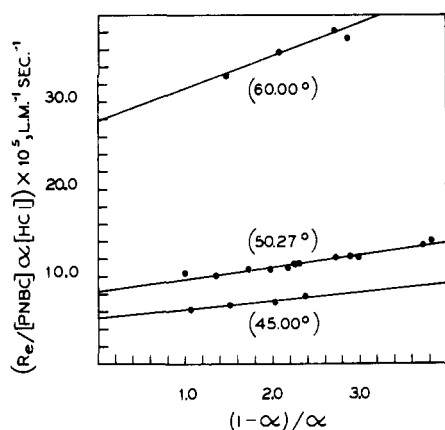(28) Reference 27, p. 28.

Figure 1. Plot of $R_e/\alpha(HCl)(PNBC)$ against $(1 - \alpha)/\alpha$ for the exchange with $p$-nitrobenzyl chloride in 82% dioxane-18% water by weight solutions.

Increasing values of $R_e/(PNBC)$ and $R_e/\alpha(HCl)\cdot(PNBC)$ with increasing hydrogen chloride concentration indicate that the reaction is neither purely first order nor purely second order. Plots of $R_e/(PNBC)$ vs. $\alpha(HCl)$ are linear for values of $\alpha(HCl)$ less than 0.00249 and have zero intercepts indicating that the first-order contribution cannot be detected in the present investigation. At values of $\alpha(HCl)$ greater than 0.00249, the slopes of the curves increase with increasing values of $\alpha(HCl)$. Because the value of $R_e$ was found to decrease with an increase in lithium perchlorate concentration (see Table I), this departure from linearity cannot be attributed to a salt effect. Plots of $R_e/\alpha\cdot(HCl)(PNBC)$ vs. $(1 - \alpha)/\alpha$, shown in Figure 1, are linear in accordance with the modified form of eq. 2 in which $k_1$ has been set equal to zero. Values of the specific rate constants, given in Table II, were calculated from these plots employing the least-squares technique.

Table II.[a] Specific Rate Constants for the Exchange of Chlorine between Hydrogen Chloride and $p$-Nitrobenzyl Chloride in 82% Dioxane-18% Water by Weight Solutions

| Temp., °C. | $k_i \times 10^4$,[b] l. mole$^{-1}$ sec.$^{-1}$ | $k_m \times 10^4$,[c] l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|
| 45.00 | 0.580 ± 0.019 | 0.093 ± 0.010 |
| 50.27 | 0.874 ± 0.022 | 0.141 ± 0.009 |
| 60.00 | 2.808 ± 0.170 | 0.370 ± 0.073 |

[a] The standard deviation is reported with each rate constant. [b] $k_i$ is the specific rate constant for the reaction of anions. [c] $k_m$ is the specific rate constant for the reaction of ion pairs.

*The Rate Law.* The Arrhenius activation energies and the frequency factors were calculated from the least-squares plots of the logarithm of the specific rate constants vs. the reciprocal of the absolute temperature. The rate of exchange, $R_e$, is well represented by the expression

$$R_e = 2.04 \times 10^{11}\alpha(HCl)(PNBC)e^{-22,600/RT} + 2.76 \times 10^8 e^{-19,600/RT}(1 - \alpha)(HCl)(PNBC) \quad (11)$$

where the units of $R_e$ are moles l.$^{-1}$ sec.$^{-1}$. The standard deviation of the activation energies given in the first and second terms of eq. 11 are 1800 and 962 cal. mole$^{-1}$,

respectively. The entropies of activation of the reaction of ions and ion pairs are $-11.4$ and $-24.5$ cal. mole$^{-1}$ deg.$^{-1}$, respectively.

## Results of Exchange Runs in Anhydrous Solvents

No exchange could be detected between hydrogen chloride and $p$-nitrobenzyl chloride in anhydrous benzene after 363 hr. at 60.00° when the concentrations of the reactants were 0.00464 and 0.950 $M$, respectively. Similarly, no exchange was observed between 0.00877 $M$ hydrogen chloride and 0.0100 $M$ benzyl chloride in benzene after 605 hr. at 24.91°.

In an attempt to determine the rate of exchange in acetone between hydrogen chloride (0.00926 $M$) and benzyl chloride (0.0102 $M$) over 856 hr. at 50.33°, it was found that the specific activity of the chloride recovered from the organic halide fraction increased with time, while the specific activity of the chloride recovered from the hydrogen chloride fraction remained relatively constant. This anomalous behavior is attributed to a reaction between hydrogen chloride and the solvent, leading to the formation of an undetermined radioactive organic halide which was subsequently recovered with the benzyl chloride fraction. Therefore, it is concluded that no exchange occurred under the aforementioned conditions.

In anhydrous dioxane, at 60.25°, the half-time for exchange between 0.00944 $M$ hydrogen chloride and 0.0473 $M$ $p$-nitrobenzyl chloride was 2246 hr. At 76.25° $p$-nitrobenzyl chloride exchanges five times faster than benzyl chloride.

The exchange between hydrogen chloride and benzyl chloride in ethanol at 76.25° proceeded with a half-time of 5 hr. when the concentration of the hydrogen chloride was 0.00946 $M$ and the concentration of benzyl chloride was 0.0456 $M$. The exchange was complicated by ethanolysis of the organic halide.

## Discussion

If a one-to-one correspondence between order and molecularity is assumed, then the results of the exchange reaction are consistent with the view that the reaction proceeds *via* concurrent bimolecular processes involving chloride ions and hydrogen chloride ion pairs. As noted by Lichten and Rao,[11] an alternative mechanism involving cation catalysis is possible, but the information available in the present work is incapable of discriminating between the two possibilities.

The direction of the observed salt effect is in accord with current theories summarized by Amis[29] and Benson.[30] In this connection it is noteworthy that the rate of displacement of chlorine from $p$-nitrobenzyl chloride by thiosulfate ion in 40% water-60% dioxane by weight decreased with an increase in ionic strength.[31] Also, the addition of sodium perchlorate decreased the rate of the second-order reaction between benzyl chloride and acetate ions in a dioxane-water mixture.[21a]

The nonexchange observed between hydrogen chloride and $p$-nitrobenzyl chloride in anhydrous benzene and acetone, solvents in which ion pairs predominate, is not in accord with the observed exchange in dioxane-

(29) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, pp. 153-174.

(30) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 536, 537.

(31) R. Fuchs and A. Nisbet, *J. Phys. Chem.*, **65**, 365 (1961).

water. This suggests that the reactivity of an ion pair is a function of the polarity of the solvent.

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## Appendix

*Effect of Hydrolysis of the Organic Halide on the Variation of the Fraction Exchange with Time.* The half-time of the exchange reactions were determined from a plot of $\ln (1 - F_{RCl})$ against time, and it is the purpose of this Appendix to show that the half-times and resulting kinetics were not affected by the hydrolysis of the organic halide. Consider the reaction

$$HCl^* + RCl = HCl + RCl^* \qquad (12)$$

taking place at a rate $R_1(t)$. Consider the chemical conversion reactions

$$HCl \longrightarrow RCl \text{ at a rate } R_2(t) \qquad (13)$$

$$RCl \longrightarrow HCl \text{ at a rate } R_2(t) + r(t) \qquad (14)$$
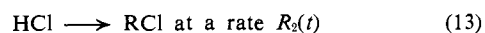
It has been shown by Luehr, Challenger, and Masters[22] that

$$\ln (1 - F_{RCl}) = -\int_0^t \frac{(a + b)R_t\, dt}{(a + \rho(t))(b - \rho(t))} \qquad (15)$$

$$\ln (1 - F_{HCl}) = -\int_0^t \frac{(a + b)R_t\, dt}{(a + \rho(t))(b - \rho(t))} + \ln \frac{a(b - \rho(t))}{b(a + \rho(t))} \qquad (16)$$

where $a$ and $b$ are the moles of HCl and RCl present at time zero; $\rho(t)$ is defined by

$$\rho(t) = \int_0^t r(t)v(t)\, dt \qquad (17)$$

where $v(t)$ is the instantaneous volume of the system (constant in the present case); and $R_t$ is given by

$$R_t = R_1(t)v(t) + R_2(t)v(t) \qquad (18)$$

Subtraction of eq. 16 from 15 gives

$$(1 - F_{RCl}) = (1 - F_{HCl}) \frac{b(a + \rho(t))}{a(b - \rho(t))} \qquad (19)$$

or

$$(1 - F_{RCl}) = (1 - F_{HCl}) \times \frac{(RCl)^0[(HCl)^0 + \Delta(HCl)]}{(HCl)^0[(RCl)^0 - \Delta(HCl)]} \qquad (20)$$

In general $F_{RCl}$ will not be equal to $F_{HCl}$.

Assume that the rate of exchange is given by

$$R_e = k_1(RCl) + k(HCl)(RCl) \qquad (21)$$

and the rate of hydrolysis by

$$-\frac{d(RCl)}{dt} = \frac{d(HCl)}{dt} = k_H(RCl) \qquad (22)$$

where $R_e$ is the rate of exchange (moles l.$^{-1}$ sec.$^{-1}$), $k_1$ is the first-order rate constant (sec.$^{-1}$), $k$ is the summation $ki\alpha + km(1 - \alpha)$ (l. mole$^{-1}$ sec.$^{-1}$), $k_H$ is the

hydrolysis constant (sec.$^{-1}$), (HCl) and (RCl) are the molar concentrations at time $t$, $\alpha$ is the degree of dissociation of hydrogen chloride, $ki$ is the second-order rate constant for ions (l. mole$^{-1}$ sec.$^{-1}$), and $km$ is the second-order rate constant for ion pairs (l. mole$^{-1}$ sec.$^{-1}$). Assuming that the hydrolysis is irreversible,[21] it follows that

$$R_t = R_1(t)v(t) = R_e v(t) \qquad (23)$$

$$a + \rho(t) = (HCl)v(t) \qquad (24)$$

$$b - \rho(t) = (RCl)v(t) \qquad (25)$$

and by substitution into eq. 21

$$R_t = k_1(b - \rho(t)) + \frac{k(a + \rho(t))(b - \rho(t))}{v(t)} \qquad (26)$$

Substitution of this value for $R_t$ into eq. 15, taking eq. 24 and 25 into consideration, yields

$$\ln = (1 - F_{RCl}) = -[(HCl)^0 + (RCl)^0]k_1 \int_0^t \frac{dt}{(HCl)} - \\ [(HCl)^0 + (RCl)^0] kt \qquad (27)$$

Since

$$(HCl) = (HCl)^0 + (RCl)^0(1 - e^{-k_H t}) \qquad (28)$$

it follows that

$$\ln (1 - F_{RCl}) = -[(HCl)^0 + (RCl)^0]k_1 \times \\ \int_0^t \frac{dt}{(HCl)^0 + (RCl)^0(1 - e^{-k_H t})} - [(HCl)^0 + \\ (RCl)^0]kt \qquad (29)$$

which can be integrated to give (notice that $F_{RCl} = 0$ when $t = 0$, and $k$ is a constant)

$$\ln (1 - F_{RCl}) = -k_1 t - \frac{k_1}{k_H} \times \\ \ln \left( \frac{(HCl)^0 + (RCl)^0 - (RCl)^0 e^{-k_H t}}{(HCl)^0} \right) - \\ [(HCl)^0 - (RCl)^0]kt \qquad (30)$$

which is the equation needed to describe the variation of the fraction exchange in the organic halide with time. For small values of $k_H t$

$$e^{-k_H t} = 1 - k_H t \qquad (31)$$

and since $\ln (1 + x) = x$ for small values of $x$, eq. 30 reduces to

$$\ln (1 - F_{RCl}) = -\frac{[(HCl)^0 - (RCl)^0]}{(HCl)^0}k_1 t - \\ [(HCl)^0 + (RCl)^0]kt \qquad (32)$$

If $k_1 = 0$, eq. 30 reduces to

$$\ln (1 - F_{RCl}) = -[(HCl)^0 + (RCl)^0]kt \qquad (33)$$

It has been shown that, if $k_H t$ is small, the plots of $\ln (1 - F_{RCl})$ against time will be linear in the case of concurrent first- and second-order reactions, and hydrolysis can be neglected. In addition, the hydrolysis has no effect on the half-time of exchange of a purely second-order reaction.