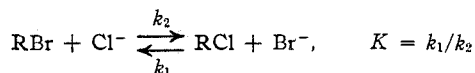


[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

**Exchange Reaction and Hydrolysis of *p*-Nitrobenzyl Bromide in Dioxane-Water Solutions<sup>1</sup>**BY JAMES W. HACKETT, O.P.,<sup>2</sup> AND HENRY C. THOMAS

The kinetics of displacement reactions between *p*-nitrobenzyl halides and lithium halides in an acetone-water mixture<sup>3</sup> and in a methanol-acetone<sup>4</sup> solution have been investigated. The rates of such reactions are well known to be greatly influenced by the nature of the solvent in which they take place. Thus the effect of varying the solvent should give some information on the character of the molecular interactions taking place in these apparently simple reactions. As a step toward obtaining more such information, a study has been made of the rates of reaction between *p*-nitrobenzyl bromide and lithium chloride in three similar solvents: three dioxane-water mixtures. The rates of the concurrent hydrolytic reactions have been measured and taken into account in the computation of the rates of the exchange reaction.

The simple exchange reaction may be written



Representing the initial concentration of the organic bromide by  $a$ , that of the chloride ion by  $b$ , and the instantaneous concentration of the products by  $x$ , the integrated rate equation is

$$k_2 = \frac{1}{At} \ln \frac{2(1-K)x - (a+b) - A}{2(1-K)x - (a+b) + A}$$

in which

$$A = \sqrt{(a+b)^2 - 4ab(1-K)}$$

The equilibrium constant is conveniently taken as  $K = k_1/k_2$ , so that  $K$  is numerically less than unity. (This choice is also made to conform with our previous usage.)

In the presence of water as a component of the solvent mixture, hydrolysis of both organic halides accompanies the exchange. These hydrolytic reactions are so predominantly in the direction of alcohol formation under the conditions of our experiments that they have been considered irreversible. It was also found by semi-quantitative measurements that the organic bromide hydrolyzed at a rate more than ten times that of the chloride. Thus the hydrolysis of the organic chloride, the product of the exchange reaction, is of little effect and was ignored for reasons of simplicity.

Retaining the significance of the symbols  $a$ ,  $b$

(1) This paper is based on the dissertation presented in 1949 to the Faculty of the Graduate School of Yale University by James W. Hackett, O.P., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Providence College, Providence, R. I.

(3) Bither, Sturtevant and Thomas, *THIS JOURNAL*, **67**, 1562 (1945).

(4) R. L. Macklin, Dissertation, Yale University (1943).

and  $x$ , the hydrolysis of the organic bromide may be handled by the introduction of a variable,  $z$ , to represent the concentration of bromide ion resulting from hydrolysis alone. The sum  $x + z$  is thus the concentration of the bromide ion produced by exchange and by hydrolysis and is the directly measured experimental quantity. The rate of the halogen exchange becomes

$$dx/dt = k_2(a - x - z)(b - x) - k_1x(x + z)$$

The rate of the hydrolysis of the organic bromide concurrent with the exchange is approximately

$$dz/dt = k_3(a - x - z)$$

in which the constant  $k_3$  is the product of the hydrolysis rate constant,  $k_h$ , and the relatively constant concentration of water. The quantity  $k_3$  was evaluated for each dioxane-water mixture, independently of the exchange reaction, by the analysis for bromide ion in solutions containing organic bromide alone. It is assumed that this value for the hydrolysis rate constant is unaffected by the presence of lithium halide in the measurement of the halogen exchange.

An exact analytical solution for the equation representing the rate of halogen exchange accompanied by hydrolysis is not known to us. The evaluation of the exchange rate constants has been carried out graphically.<sup>5</sup> The rate equation written in the integrated form may be arranged as

$$1 + k_1 \frac{\int_0^t x(x+z)dt}{x} - k_2 \frac{\int_0^t (a-x-z)(b-x)dt}{x} = 0$$

This is the equation of a straight line in

$$m = \frac{\int_0^t x(x+z)dt}{x} \quad \text{and} \quad n = \frac{\int_0^t (a-x-z)(b-x)dt}{x}$$

with intercepts  $m_0 = -1/k_1$  and  $n_0 = 1/k_2$  and with slope  $k_1/k_2 = K$ . The bromide ion concentration,  $x + z$ , was obtained by analysis of water extracts of the reaction samples. That part of the bromide ion concentration resulting from hydrolysis was calculated by graphical integration of the expression

$$z = k_3 \int_0^t (a - x - z)dt$$

using the analytical data of the exchange experiments and the independently evaluated  $k_3$ . Finally,  $m$  was plotted against  $n$  and the resulting line extrapolated to the intercepts. Actually, to make the extrapolation objective, the method of least squares was used. Values were thus ob-

(5) We are indebted to Prof. Lars Onsager for the suggestion of this procedure.

tained for  $k_2$ ,  $k_1$ , and  $K$ . A typical pair of curves so obtained is given in Fig. 1. The fact that the experiments are designed to determine  $k_2$  finds its expression in the character of the extrapolations of the  $m$ - $n$  curves. The  $n$  intercept,  $1/k_2$ , is proximate to the plotted quantities and is relatively insensitive to small experimental uncertainties. The  $m$  intercept,  $-1/k_1$ , is obtained by a considerable extrapolation of the experimental data and is subject to greater uncertainty. The present work does not produce reliable values for  $k_1$ .

### Experimental

Eastman Kodak Co. White Label *p*-nitrobenzyl bromide was purified by recrystallization from 90% alcohol. Lithium chloride was prepared from Baker's "Analyzed" lithium carbonate.<sup>6</sup> Eimer and Amend diethylene oxide was purified over sodium,<sup>7</sup> distilled, and three times crystallized. The melting point of the product, 11.75°, was within 0.03° of that given in the literature.

Dioxane-water solutions were prepared by weight; the composition of the solutions was considered known to  $\pm 0.05\%$ .

A reaction series was carried out as follows: A lithium chloride solution in the appropriate solvent, a calibrated 500-ml. volumetric flask containing a weighed quantity of *p*-nitrobenzyl bromide, and a third empty glass-stoppered flask of convenient shape for pipetting were brought to temperature equilibrium in the thermostat. Slightly less than 500 ml. of the lithium chloride solution was added to the volumetric flask and the bromide dissolved by vigorous shaking. The reaction was timed from this addition. After adjusting to 500 ml. the solution was transferred to the third flask. A sample was immediately taken for a Volhard titration to determine the initial chloride content of the solution. At timed intervals, samples of approximately 50 ml. were removed by means of a fast-running pipet and delivered into flasks containing 35 ml. each of benzene and water to quench the reaction. The weights of the samples were determined by weighing the quenching flasks. Volume concentrations were obtained using density measurements made on each solution at the reaction temperature.

Separation of the organic and inorganic reactants and products was effected by extraction with benzene and appropriate careful washing of the benzene and water solutions. The total water extract was reduced in volume and titrated for bromide by the method of Lang.<sup>8</sup>

The thermostats were controlled to within 0.02° at 60° and 30°, and to within 0.2° at 5°. Reaction times were measured with an electric clock having a seconds indicator. The intervals varied from thirty minutes to several days.

The reproducibility of the results is apparent from the data depicted in Fig. 1. The mean square deviation of the experimental points from the  $m$ - $n$  lines indicates a maximum probable error of 6% in  $k_2$ . In all cases at least two series of determinations were made at each temperature in each of the three solvents. In one, the concentration ratio of the reactants was approximately 2; in the other, approximately 0.5. The average agreement of the experimentally determined constants is 6%, the differences varying from 1 to 15%.

The hydrolysis reactions in the absence of lithium salts were followed in an essentially similar manner. Bromide was determined by the Volhard titration. Freshly prepared solutions of the organic bromide gave evidence of no free halide ion.

### Results and Discussion

The results of our experiments are summarized as velocity constants in Tables I and II. The

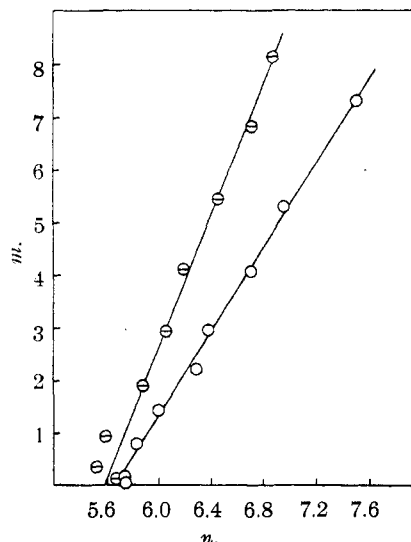


Fig. 1.—Typical pair of  $m$ - $n$  curves obtained in the evaluation of the rate constants for the exchange reaction.

temperature coefficients of the reactions and interpolated values of the rate constants at 25° were

Temp., °C.	Weight per cent. dioxane		
	90.0	70.0	50.0
60	110	350	870
30	13	18	40
5	1.0	1.8	2.8

Temp., °C.	Weight per cent. dioxane		
	90.0	70.0	50.0
60	295	425	397
30	22.8	35.7	25.2
5	1.80	2.64	1.93

Wt. % dioxane	90.0	70.0	50.0
Dielectric constant	5.61	17.69	34.26

The Hydrolysis Reaction			
$k_2 \times 10^8$ (liters/mole sec.)	0.7	1.4	2.7
$\Delta H$ (kcal./mole)	15.4	17.2	18.8
$\Delta F$ (kcal./mole)	28.6	28.2	27.8
$-\Delta S$ (cal./mole-deg.)	44.2	36.8	30.1
The Exchange Reaction			
$k_2 \times 10^4$ (liters/mole sec.)	1.43	2.13	1.63
$\Delta H$ (kcal./mole)	16.5	16.4	17.2
$\Delta F$ (kcal./mole)	22.7	22.5	22.6
$-\Delta S$ (cal./mole-deg.)	20.8	20.3	18.1

(9) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 117.

(6) Booth, "Inorganic Syntheses," Vol. I, p. 1.

(7) Kraus and Vingee, THIS JOURNAL, 56, 511 (1934).

(8) Lang, Z. anorg. Chem., 144, 75 (1925).

obtained from appropriate plots of the data. These results are summarized for both the hydrolysis and exchange reactions in Table III.

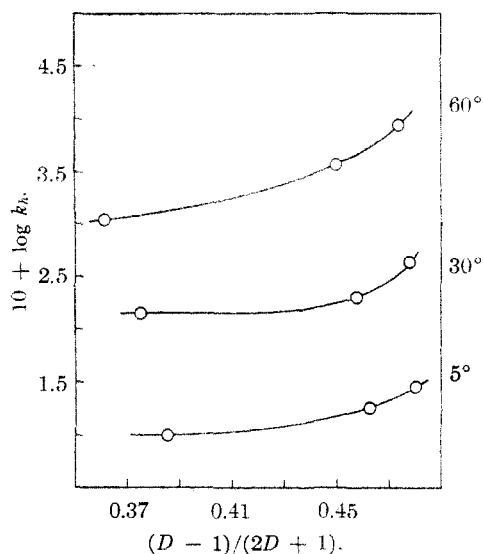


Fig. 2.—Dependence of hydrolysis rate constants on the dielectric constant of the solvent.

**The Hydrolysis Reaction.**—In Fig. 2 are given plots of the hydrolysis constants as calculated according to the simple theory for reactions between dipolar molecules.<sup>10</sup> It should be noted that these values of the hydrolysis constant have been computed from the constant  $k_3$  and the total molar concentration of water. Since the physical properties of dioxane-water mixtures<sup>11,12,13</sup> point to the existence of an addition complex, the actual concentrations of free water may be much less than the values used. Particularly with the dioxane-rich solutions we obtain values of  $k_h$  much too small. It is probable that the addition complex itself may enter into the hydrolysis reaction. We would be thus led to consider at least two independent reaction paths. Without more information on the nature of these solutions, no reasonable discussion can be given to explain the shapes of the curves of Fig. 2. In particular, the large differences between the entropies of activation for the hydrolysis in the different solvents (Table III) have doubtful physical significance. However, the use of the constant  $k_3$  to correct for the hydrolysis during the course of the exchange reaction remains a perfectly legitimate procedure.

**The Exchange Reaction.**—The effect of the solvent on the rates of the exchange reaction is summarized in the curves of Fig. 3. Here are plotted the values of  $\log k_e$  against  $1/D$  as abscissas. In dioxane-rich solvents the reactant

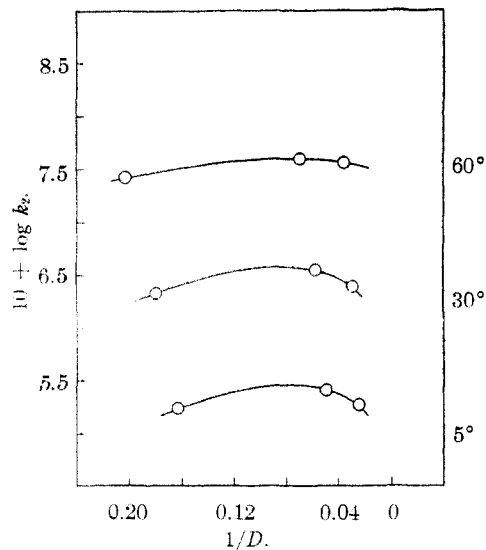


Fig. 3.—Dependence of exchange rate constants on the dielectric constant of the solvent.

lithium chloride is present in great part as associated ion pairs,<sup>14</sup> *i. e.*, dipoles of large moment. Thus, in this region, we may expect an increase in rate with increasing dielectric constant. As the water content of the solution increases, the dissociation of the ion pairs increases and is complete at approximately fifty weight per cent. Here we are dealing with a dipole-ion reaction, for which we expect a decrease in rate with increasing dielectric constant.<sup>15</sup> These competing effects are apparent from the existence of the maxima of the curves (Fig. 3). The fact that the curves become flatter at the higher temperatures is in accord with theoretical expectations.

#### Summary

The exchange reaction between *p*-nitrobenzyl bromide and lithium chloride has been investigated in 90, 70 and 50% by weight aqueous dioxane at 60, 30 and 5°.

The specific rate constants for the hydrolysis of *p*-nitrobenzyl bromide were determined independently in the solvent mixtures at the several temperatures.

Applying corrections for concurrent hydrolysis, the specific reaction rate constants for the exchange reaction were evaluated by a method of graphical integration.

Standard thermodynamic quantities for the formation of the activated complex of the hydrolysis and of the exchange reaction were obtained from the experimental data.

The observed dielectric constant effect of the reaction media was found to be in substantial agreement with predicted behavior for the exchange reaction.

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(10) Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 419.

(11) "Annual Tables of Physical Constants," (1943-1944) p. 13.

(12) Hovorka, Schaefer and Dreisbach, *THIS JOURNAL*, **58**, 2264 (1936).

(13) Weith, Hobbs and Gross, *ibid.*, **70**, 805 (1948).

(14) Fuoss, *Chem. Rev.*, **17**, 27 (1935).

(15) Glasstone, Laidler and Eyring, *loc. cit.*, p. 439.