[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

The Exchange Reaction between Substituted Benzyl Iodides and Potassium Iodide. I. Benzyl Iodide[1]

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A measurable exchange has been observed in methyl alcohol and ethyl alcohol between the iodine atom in benzyl iodide and the iodide ion in potassium iodide. The exchange reaction was investigated over a temperature range from 0 to 44°. The total iodide concentration in methanol and in ethanol ranged from 0.00275 to 0.0314 *M* and 0.00374 to 0.0269 *M*, respectively. The rate laws for the exchange reaction are $R = 5.9 \times 10^{11}e^{-16,200/RT}$ (BzI)(KI) in methyl alcohol and $R = 7.1 \times 10^{12} e^{-17,300/RT}$ (BzI)(KI) in ethyl alcohol, where the units of R are moles liter^{-1} min.$^{-1}$.

Introduction

The investigation of the effects of structure and solvent on the kinetics of metathetical reactions such as the hydrolysis of alkyl halides led Ingold and Hughes and their collaborators to postulate the concept of duality of mechanism for the nucleophilic displacement reaction.[3] Subsequently the kinetics of the isotopic exchange reactions between various halogenobenzenes, aliphatic and benzyl halides and halide salts in various solvents have been studied.[4] The exchange reaction is particularly suitable for this type of study because the accompanying enthalpy change is essentially zero and the composition of the reaction mixture remains constant during the course of the reaction. We have undertaken an investigation of the exchange reaction between substituted benzyl iodides and potassium iodide in different solvents. It is hoped that as a result of these studies important information may be obtained regarding the influence of solvent and substituent on the mechanism and rate of the nucleophilic displacement reaction on carbon. This paper deals with the exchange between benzyl iodide and potassium iodide in methanol and ethanol. In each solvent the reaction was found to be first order with respect to both the benzyl iodide and potassium iodide.

Experimental

Radioactivity.—The 8.0-day I^{131} was used as tracer in all experiments. The I^{131} was extracted from neutron-irradiated tellurium metal according to the procedure of Kenney and Spragg[5] with the exception that a small amount of inactive potassium iodide was added during the oxidation step. The active aqueous iodide solution thus obtained was acidified with sulfuric acid, treated with an excess of potassium dichromate and extracted with benzene. The benzene phase was washed several times with water and then shaken with an aqueous solution of potassium iodide. The resulting active potassium iodide solution was evaporated to dryness and the residue dissolved in either methanol or ethanol.

In addition to the chemical procedure, evidence for the purity of the iodine activity was obtained by observing the decay of a representative sample of an active iodide solution over a period of five half-lives. The activity decayed with an 8.0-day half-life in satisfactory agreement with that reported in the literature.[6]

Chemicals.—Benzyl iodide was prepared by allowing Eastman Kodak chlorine-free benzyl alcohol to react with concentrated aqueous hydriodic acid.[7] The crude product was dried for 24 hours over Drierite and then distilled twice under 9.5 mm. pressure. The final distillate was washed with a 2% solution of sodium bisulfite and water. The washed product was dried with anhydrous magnesium sulfate, decanted at 25° into a glass-stoppered flask and stored in the dark at 10°. Analysis of the final product yielded 99.9% benzyl iodide on the basis of the iodine content.

Mallinckrodt absolute methanol and U. S. Industrial Chemicals, Inc., absolute ethanol were treated with magnesium methoxide and magnesium ethoxide, respectively.[8] Nitrogen was passed through each solvent, prior to use, to remove dissolved oxygen.

All other chemicals were of Analytical Reagent Grade.

Procedure.—Solutions of benzyl iodide and active potassium iodide were brought to reaction temperature, mixed, and then placed in a constant temperature (±0.1°) water-bath. After a given interval of time, the reactants were separated and the radioactivity present in each reactant determined. When the expected half-time for exchange was less than one hour, separate reaction mixtures were prepared for each reaction-time interval. For longer half-times of exchange aliquots were removed from a reaction mixture at successive time intervals. All exchange reactions were carried out in the absence of light.

The concentrations of the benzyl iodide and potassium iodide solutions were ascertained through determination of the iodine content of each solution according to the Volhard method.[9] Since all solutions were prepared at room temperature it was necessary to correct the analytically determined concentrations for the volume change of the solutions when the reaction temperature was lower or higher than room temperature.

Separation Procedure.—The reactants were separated by shaking 2 ml. of the reaction mixture with 2 ml. of benzene and 2 ml. of water. A two-phase system resulted; the benzene phase contained the benzyl iodide; the potassium iodide was in the aqueous phase. The two phases were separated by centrifugation. The quantity of benzyl iodide extracted into the aqueous phase was very small as indicated by the failure of a silver iodide precipitate to form upon addition of silver nitrate to the aqueous phase of a separation in

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[2] (a) This paper is a portion of the dissertation presented by Paul Stillson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1951; (b) Research Corporation Fellow, 1950–1951.

[3] (a) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941); (b) J. W. Baker, *ibid.*, **37**, 632 (1941), (these papers review the theory and contain numerous pertinent references.)

[4] (a) A. C. Wahl and N. A. Bonner, Editors, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951. See Table 1A, Part II, for a summary of work reported up through 1949; (b) S. Sugden and J. B. Willis, *J. Chem. Soc.*, 1360 (1951); (c) M. B. Neiman and Yu. M. Shapovalov, *Doklady Akad. Nauk S.S.S.R.*, **77**, 423 (1951); (d) V. B. Miller, M. B. Neiman and Yu. M. Shapovalov, *ibid.*, **75**, 419 (1950); (e) R. D. Heyding and C. A. Winkler, *Can. J. Chem.*, **29**, 790 (1951); (f) S. F. Van Straten, R. V. V. Nichols and C. A. Winkler, *ibid.*, **29**, 372 (1951); (g) G. W. Hodgen, H. G. V. Evans and C. A. Winkler, *ibid.*, **29**, 60 (1951); (h) A. M. Kristjanson and C. A. Winkler, *ibid.*, **29**, 154 (1951); (i) S. May and B. Giraudel, *Compt. rend.*, **234**, 326 (1952); (j) S. May and B. Giraudel *ibid.*, **234**, 2280 (1952); (k) S. May, M. Sarraf, A. Vobaure and P. Daudel, *ibid.*, **233**, 744 (1951); (l) S. May, P. Daudel, J. Schottey, M. Sarraf and A. Vobaure, *ibid.*, **232**, 727 (1951).

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[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1946, p. 572.

which the potassium iodide was omitted. However, some (1-3%) potassium iodide extracted into the benzene phase and, therefore, it was necessary to apply a small correction to the activity in the benzene phase. The fraction of potassium iodide extracted was independent of the potassium iodide concentration but varied slightly with the solvent used and the temperature.

Measurement of Radioactivity.—The iodine activity in each phase was determined by detection of the high-energy gamma radiation associated with the decay of I^{131}[10] with a thick-walled copper Geiger-Müller tube according to the procedure of Keneshea and Kahn.[11] All counting samples had activities within the range from 60 to 2000 counts per minute, and in this range the response of the counter was linear.

Errors.—The error in the correction for radioactive decay was small because samples to be intercompared were counted within a few hours of one another. The main sources of experimental error were the uncertainty in the concentration of the solutions (*ca.* ± 0.5%), the uncertainty in the fraction of potassium iodide extracted into the benzene phase during the separation procedure (*ca.* ± 1%), the uncertainty in the reaction time (*ca.* ±0.5%), the uncertainty in the calibration of the counting tubes (*ca.* ±1%), and the statistical fluctuations in the counting rate (*ca.* ±1%). The probable error in the rate constants is thought not to be greater than 4%.

Results and Discussion

The reaction investigated is

$$\text{BzI} + \text{KI}^* = \text{BzI}^* + \text{KI}$$

where the asterisks indicate radioactive atoms. The logarithmic form of the first-order exchange law[12] for this particular reaction is

$$-\ln(1 - F) = \frac{R[(\text{BzI}) + (\text{KI})]t}{(\text{BzI})(\text{KI})} \qquad (1)$$

where

(BzI) = total concn. (active and inactive) of benzyl iodide in moles per liter

(KI) = total concn. (active and inactive) of potassium iodide in moles per liter

F = fraction exchange at time t, = specific activity of benzyl iodide at time t, divided by the equilibrium specific activity of benzyl iodide (specific activity of benzyl iodide at time $t = \infty$) where the specific activity of benzyl iodide = 0 at time $t = 0$

R = actual rate at which the exchange of iodine atoms between benzyl iodide and potassium iodide takes place. For any one experiment, R will be constant because (BzI) and (KI) are constant

According to equation (1), a plot of log(1 − F) *vs.* time should give a straight line passing through 1.0 at zero time regardless of the mechanism. A typical set of data are plotted in Fig. 1.

Separation-induced exchange[13] was absent within experimental error. This is indicated by the fact that the curves of the type shown in Fig. 1 extrapolate to zero fraction exchange at zero time as is required by the first-order exchange law.

When 50% exchange has taken place, $F = {}^1/_2$ and $t = t^{1/2}$ by definition. Substitution of ${}^1/_2$ for (1 − F) and $t^{1/2}$ for t in equation (1) gives

$$R = \frac{(\text{BzI})(\text{KI}) \ln 2}{[(\text{BzI}) + (\text{KI})]t_{1/2}}$$

Since in any one run (BzI) and (KI) are known, it is possible to evaluate R, the rate of exchange, for this particular run after having determined $t_{1/2}$, the half-time for exchange, from a plot of log (1 − F) *vs.* t.

If the exchange reaction is first order with respect to benzyl iodide and potassium iodide, an S_N2-type reaction, $R = k_1(\text{BzI})(\text{KI})$, and a plot of $R/(\text{BzI})$ *vs.* (KI) should yield a straight line passing through the origin with a slope equal to k_1, the specific reaction rate. If the rate-determining step of the exchange reaction is the ionization of benzyl iodide, an S_N1-type reaction, $R = k_2$ (BzI), and a plot of $R/(\text{BzI})$ *vs.* (KI) should yield a straight line parallel to the (KI) axis with intercept on the $R/(\text{BzI})$ axis equal to k_2, the specific reaction rate. If the exchange reaction takes place through both of the aforementioned paths, $R = k_1(\text{BzI})(\text{KI}) + k_2(\text{BzI})$, and a plot of $R/(\text{BzI})$ *vs.* (KI) should yield a straight line with a slope and intercept equal to the respective specific reaction rates for the two paths. The data of Tables I and II are plotted in Fig. 2. It is seen that in both solvents, there is no evidence for the S_N1-type reaction. The type of straight line plot shown in Fig. 2 will be obtained for any rate law in which the sum of the two exponents is 2, provided the ratio of the reactant concentrations is maintained constant. Aside from the 0 and 44° runs in methanol the ratios of the reactant concentrations differ sufficiently so that the corresponding straight line plots can be taken as evidence for the

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS IN METHANOL

Temp., °C.	$C_6H_5CH_2I$ concn., *f*	KI concn., *f*	$t^{1/2}$, min.	$R \times 10^5$, mole- liter^{-1} min.$^{-1}$	k, mole^{-1} liter min.$^{-1}$
0.0	0.01182	0.01182	453	0.91	0.064
.0	.00434	.00440	1368	0.111	.058
.0	.01526	.01614	366	1.49	.060
.0	.00910	.00915	637	0.50	.058
27.3	.00451	.00360	95.5	1.45	.89
27.3	.00612	.00660	60	3.63	.90
27.3	.00287	.00224	144	0.60	.94
27.3	.01040	.00726	44.5	6.67	.88
44.0	.00143	.00132	66.5	0.72	3.78
44.0	.00375	.00395	23.3	5.72	3.86

TABLE II

RESULTS OF EXCHANGE EXPERIMENTS IN ETHANOL

Temp., °C.	$C_6H_5CH_2I$ concn., *f*	KI concn., *f*	$t^{1/2}$, min.	$R \times 10^5$, mole. liter^{-1} min.$^{-1}$	k, mole^{-1} liter min.$^{-1}$
0.0	0.01311	0.01065	306	1.33	0.096
.0	.01413	.01275	270	1.36	.096
.0	.01146	.00819	358	0.92	.099
.0	.00901	.00256	574	0.239	.105
27.3	.00311	.00250	72.5	1.33	1.71
27.3	.00672	.00371	39.3	4.21	1.70
27.3	.01020	.00736	23.5	12.6	1.68
27.3	.00370	.00219	66.0	1.45	1.78
44.0	.00127	.000796	39.0	0.87	8.61
44.0	.00305	.00264	14.5	6.77	8.40
44.0	.00235	.00181	19.5	3.62	8.46
44.0	.00225	.00149	22.0	2.82	8.44
44.0	.00248	.00205	18.5	4.20	8.29

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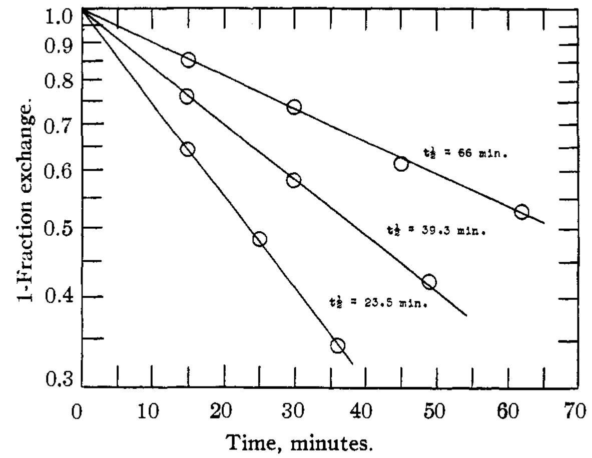

Fig. 1.—Semi-logarithmic plot of (1-fraction exchange) against time for experiments in ethanol at 27.3°.

first-order dependence on each reactant. It is reasonable to assume that the rate law for the reaction in methanol at 0 and 44° will also be first order with respect to each reactant.

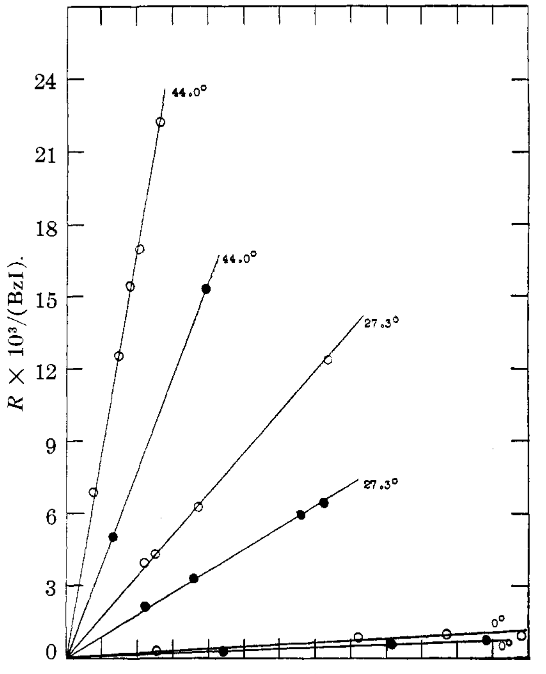

Fig. 2.—Dependence of the ratio R/(BzI) on the potassium iodide concentration in methanol (●) and in ethanol (○).

The Activation Energies.—The curves shown in Fig. 3 are semilogarithmic plots of the average values for the specific reaction rate k_1 against the reciprocal of the absolute temperature. The experimental activation energies for the exchange reaction in methanol and ethanol as determined from these plots are 16,200 ± 500 and 17,300 ± 500 cal., respectively.

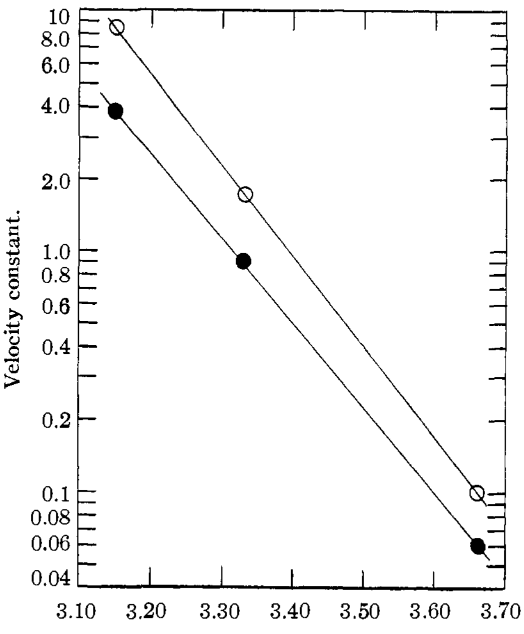

Fig. 3.—The temperature dependence of the exchange reaction in methanol (●) and in ethanol (○).

The Rate Laws.—From the foregoing discussion it appears that the exchange reaction is first order with respect to both the benzyl iodide and potassium iodide concentrations in methanol and ethanol over a temperature range from 0 to 44°. The total iodide concentration ranged from 0.0314 to 0.00275 M and 0.00374 to 0.0269 M, respectively. The rate laws for the exchange reaction are

$$R = 5.9 \times 10^{11}e^{-16,200/RT}(\mathrm{BzI})(\mathrm{KI}), \text{ (in methanol)}$$
$$R = 7.1 \times 10^{12}e^{-17,300/RT}(\mathrm{BzI})(\mathrm{KI}), \text{ (in ethanol)}$$

where the units of R are moles liter^{-1}min.$^{-1}$.

Effect of Solvent on Rate of Exchange.—The specific reaction rate of the exchange reaction is less in methanol than in ethanol. This observation is in accord with the theory of Laidler and Eyring[14] which states that the rate of an ion–molecule reaction should decrease with increase in dielectric constant of the solvent. The values for the dielectric constants for methanol[15] and ethanol[16] at 25° are 32.66 and 24.26, respectively.

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