subsequent reactions of the primary and secondary products above.[15]

The most important feature of the mechanism proposed is that the primary step is the rupture of a carbon–chlorine bond, not the carbon–hydrogen bond. The latter possibility was ruled out since a much larger isotope effect on the rate should have been observed when comparing a carbon–hydrogen with a carbon–deuterium bond scission. Newton and Rollefson,[22] who measured the relative rates of photochlorination of chloroform and chloroform-*d*, found a large isotope effect attributed to the step $Cl\cdot + CCl_3H \rightarrow CCl_3\cdot + HCl$. The result of the exchange experiment between chloroform-*d* and hydrogen chloride suggest that this step is a reversible one, confirming the opinion of Newton and Rollefson,[22] who found that chlorination of chloroform in the presence of deuterium chloride yielded some chloroform-*d*. A similar reaction between methyl radicals and hydrogen chloride has been reported.[23]

Catalysis by tetrachloroethylene is not easily explained, however. A possibility would seem to be the removal of trichloromethyl radicals, as[24]

$$CCl_3\cdot + C_2Cl_4 \longrightarrow CCl_3CCl_2CCl_2\cdot \qquad (A)$$

$$CCl_3\cdot + \cdot CCl_2CCl_2CCl_3 \longrightarrow 2C_2Cl_5\cdot \qquad (B)$$

$$C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl\cdot \qquad (C)$$

A more detailed discussion of the mechanism of the thermal decomposition of chloroform will appear in the forthcoming paper "II. Kinetics."

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(15) For example, vinyl chloride could arise from the pyrolysis of methylene chloride through a mechanism which involves abstraction, $Cl\cdot + CCl_2H_2 \rightarrow CCl_2H\cdot + HCl$ and the recombinations $2CClH_2\cdot \rightarrow C_2Cl_2H_4$, $2CCl_2H\cdot \rightarrow C_2Cl_4H_2$. Dehydrochlorination now gives vinyl chloride in one case and trichloroethylene in the other. Trichloroethylene was found as a product in the pyrolysis of methylene chloride. Several of the reactions in Table IV have received attention from other workers. Barton[16] examined the pyrolysis of pentachloroethane at 550° and Barton and Howlett[17] studied the dehydrochlorination of the isomeric tetrachloroethanes, giving some attention to the decomposition of trichloroethylene. Tetrachloroethylene is very stable toward polymerization.[18a, 18b] Williams[5] studied the dehydrochlorination of 1,1,2-trichloroethane, and Howlett[19] reported on the decomposition of 1,2-dichloroethane. The dimerization and polymerization of trichloroethylene has been studied by Henne and Ruh,[20] and by Schmerling and West.[18a] Dainton and Ivin[21] studied the pyrolysis of hexachloroethane.

(16) D. H. R. Barton, *J. Chem. Soc.*, 148 (1949).

(17) D. H. R. Barton and K. E. Howlett, *ibid.*, 2033 (1951).

(18) (a) L. Schmerling and J. P. West, THIS JOURNAL, **71**, 2015 (1949); (b) V. V. Korshak and N. G. Matveeva, *Doklady Akad. Nauk S.S.S.R.*, **85**, 797 (1952); *C. A.*, **47**, 28i (1953).

(19) K. E. Howlett, *Trans. Faraday Soc.*, **48**, 25 (1952).

(20) A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

(21) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 295 (1950).

(22) T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

(23) R. J. Cvetanovic and E. W. R. Steacie, *Can. J. Chem.*, **31**, 158 (1953).

(24) The alternative, removal of hydrogen chloride, appears unlikely, since it is known[25] that hydrogen chloride will not add homogeneously in the gas phase to alkenes. On the other hand Schmerling and West[18a] found that in the benzoyl peroxide-induced addition of hydrocarbons to tetrachloroethylene, the yield of addition products decreased as the temperature was increased from 115 to 160°. In the present study no propanes were among the products, hence the addition of trichloromethyl radicals to tetrachloroethylene must be considered to lead to further reactions not regenerating trichloromethyl radicals.

(25) G. B. Kistiakowsky and C. H. Stauffer, THIS JOURNAL, **59**, 165 (1937).

CHICAGO, ILL.

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

The Exchange Reaction between Substituted Benzyl Iodides and Potassium Iodide. II. *p*-Nitrobenzyl Iodide[1]

BY E. LEE PURLEE, MILTON KAHN AND J. L. RIEBSOMER

RECEIVED MARCH 13, 1954

A measurable exchange has been observed in methanol and ethanol between the iodine atom in *p*-nitrobenzyl iodide and the iodide ion in potassium iodide. The exchange reaction was investigated over a temperature range from 0 to 30.9°. The total iodide concentration in methanol and in ethanol ranged from 0.000986 to 0.00609 M and 0.000983 to 0.00599 M, respectively. The rate laws for the exchange reaction are $R = 3.60 \times 10^{11}e^{-15,570/RT}(p\text{-}NO_2BzI)(KI)$ in methanol and $R = 5.42 \times 10^{12}e^{-16,460/RT}(p\text{-}NO_2BzI)(KI)$ in ethanol, where the units of R are moles liter^{-1} min.$^{-1}$.

Introduction

This paper represents the second in a series[2] of studies designed to obtain information regarding the influence of solvent and substituent on the mechanism and rate of the nucleophilic displacement reaction on carbon. The kinetics of the exchange reaction between *p*-nitrobenzyl iodide and potassium iodide in methanol and ethanol have been investigated. In each solvent the reaction was found to be first order with respect to both the *p*-nitrobenzyl iodide and potassium iodide.

Experimental

Radioactivity.—The 8.0-day I^{131} which was used as tracer in all experiments was extracted from neutron-irradiated tellurium metal. Solutions of potassium iodide in methanol and ethanol containing I^{131} activity were prepared as described previously.[2]

Chemicals.—*p*-Nitrobenzyl iodide was prepared according to the method of Finkelstein.[3] The crude product was twice crystallized from acetone and subsequently crystallized four times from absolute ethanol. Analysis of the product by the Volhard method of iodide determination[4]

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(1) This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fulfillment of the requirements for the degree of Master of Science, in the Graduate School of the University of New Mexico, February, 1952, by E. Lee Purlee.

(2) P. Stillson and M. Kahn, THIS JOURNAL, **75**, 3579 (1953).

(3) H. Finkelstein, *Ber.*, **43**, 1531 (1910).

(4) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1946, pp. 475, 573.

rendered an iodide content of 48.18% *versus* that calculated, 48.28%. Qualitative tests for trace amounts of free bromine[5] were negative.

Absolute methanol and absolute ethanol were prepared from "absolute" C.P. grade reagents according to the method of Lund and Bjerrum.[6] Nitrogen was passed through each solvent, prior to use, to remove dissolved oxygen.

All other chemicals used were of Analytical Reagent Grade.

Procedure.—Solutions of *p*-nitrobenzyl 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, an aliquot was removed from the reaction mixture, the reactants separated, and the radioactivity in each reactant determined. All exchange reactions were carried out in the absence of light.

The concentration of a potassium iodide solution was determined according to the Volhard method.[4] Solutions of *p*-nitrobenzyl iodide were prepared by dissolving a known amount of the solid in appropriate volumes of solvent.

Since all solutions were prepared at 20° it was necessary to correct the analytically determined concentrations for the volume change of the solution when the reaction temperature was lower or higher than 20°. These corrections were calculated from expressions for the cubical coefficients of expansion for the solvents.[7]

The reactants were separated according to the procedure previously reported.[2]

Measurement of Radioactivity.—The high-energy gamma radiation associated with the decay[8] of I^{131} was detected with a scintillation counter employing a #5819 R.C.A. phototube and a thallium activated sodium iodide crystal. Liquid samples were prepared according to the procedure of Keneshea and Kahn.[9]

Results and Discussion

The reaction investigated is

$$p\text{-NO}_2\text{BzI} + \text{KI}^* = p\text{-NO}_2\text{BzI}^* + \text{KI}$$

where the asterisks indicate radioactive atoms. The logarithmic form of the first-order exchange law[10] for this particular reaction is

$$-\ln(1 - F) = \frac{R[(p\text{-NO}_2\text{BzI}) + (\text{KI})]t}{(p\text{-NO}_2\text{BzI})(\text{KI})} \quad (1)$$

where

R = actual rate at which the exchange of iodine atoms between *p*-nitrobenzyl iodide and potassium iodide takes place
(KI) = total concn. (active and inactive) of potassium iodide in moles/l.
(p-NO$_2$BzI) = total concn. (active and inactive) of *p*-nitrobenzyl iodide in moles/l.
F = fraction exchange at time t.

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

$$R = \frac{(p\text{-NO}_2\text{BzI})(\text{KI})\ln 2}{[(p\text{-NO}_2\text{BzI}) + (\text{KI})]t_{1/2}}$$

Since in any one run (p-NO$_2$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.

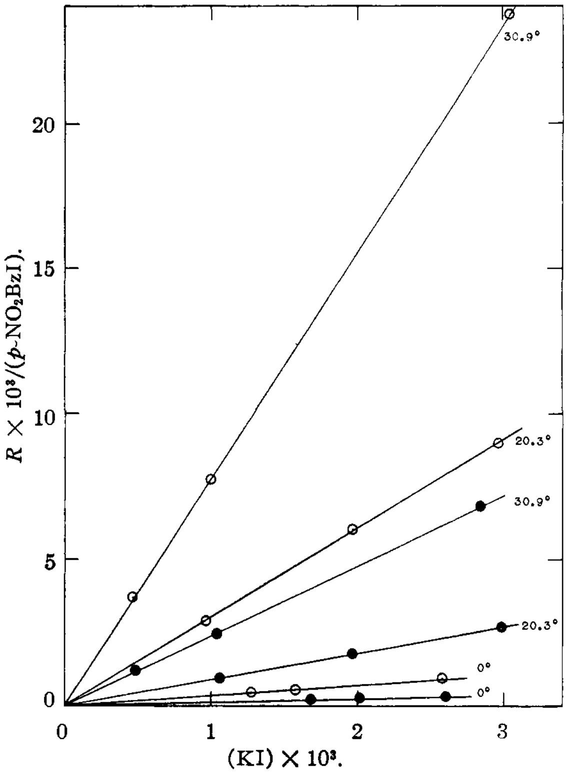

Fig. 1.—Dependence of the ratio $R/(p\text{-NO}_2\text{BzI})$ on the potassium iodide concentration in methanol (●) and in ethanol (O).

If the exchange reaction is first order with respect to *p*-nitrobenzyl iodide and potassium iodide,

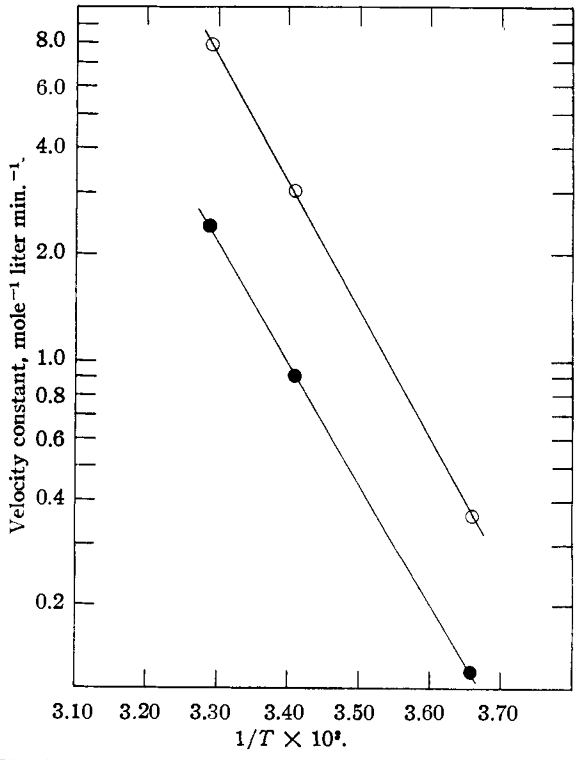

Fig. 2.—The temperature dependence of the exchange reaction in methanol (●) and in ethanol (O).

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(5) S. M. McElvain, "Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, pp. 40–42.

(6) H. Lund and N. Bjerrum, *Ber.*, **64**, 210 (1931).

(7) N. A. Lange, "Handbook of Chemistry," 6th edition, Handbook Publishers, Inc., Sandusky, Ohio, 1946.

(8) F. Metzger and M. Deutsch, *Phys. Rev.*, **74**, 1640 (1948).

(9) F. J. Keneshea, Jr., and M. Kahn, THIS JOURNAL, **74**, 5254 (1952).

(10) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 285 ff.

an SN2-type reaction, $R = k(p\text{-NO}_2\text{BzI})(\text{KI})$, and a plot of $R/(p\text{-NO}_2\text{BzI})$ *vs.* (KI) should yield a straight line passing through the origin. The data are plotted in Fig. 1. It is seen that in both solvents, as discussed elsewhere,[2] there is no evidence for the SN1-type reaction.

The Activation Energies.—The curves shown in Fig. 2 are semi-logarithmic plots of the average values for the specific reaction rate constant k 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 15,570 ± 200 cal. and 16,460 ± 200 cal., respectively.

It is of interest to compare the above activation energies with the values 16,200 and 17,300 cal. obtained for the exchange reaction between benzyl iodide and potassium iodide[2] in methanol and ethanol, respectively. The observed decrease in activation energy accompanying the substitution of a nitro group for hydrogen in the *para* position is consistent with the observation that, in general, the increase in positive character of the carbon atom being attacked, more than compensates for the concomitant tightening of the C–I bond when the attacking agent is an ion.[11]

The Rate Laws.—From the foregoing discussion it is reasonable to assume that the exchange reaction is first order with respect to both the potassium iodide and p-nitrobenzyl iodide concentrations in methanol and ethanol over a temperature range from 0 to 30.9°. The total iodide concentration ranged from 0.000986 to 0.00609 M and 0.000983 to 0.00599 M, respectively. The rate laws for the exchange reaction are

$$R = 3.60 \times 10^{11} e^{-15{,}570/RT}(p\text{-NO}_2\text{BzI})(\text{KI}) \text{ (in methanol)}$$
$$R = 5.42 \times 10^{12} e^{-16{,}460/RT}(p\text{-NO}_2\text{BzI})(\text{KI}) \text{ (in ethanol)}$$

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

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[11] J. W. Baker, *Trans. Faraday Soc.*, **37**, 632 (1941).

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[CONTRIBUTION FROM INSTITUUT VOOR KERNPHYSISCH ONDERZOEK, 18 OOSTERRINGDIJK, AMSTERDAM]

The Exchange of Iodine between Organic Iodides and Inorganic Iodine in Aqueous Solution

BY H. v. d. STRAATEN AND A. H. W. ATEN, JR.

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With I^{131} as a tracer reaction rates of the iodine exchange between iodoacetic acid, the sodium salt and the methyl ester of this acid and iodide ions have been determined. The exchange of iodine between iodoacetic acid and free iodine or triiodide ions is much slower than it is with the monoiodide.

Introduction

The exchange between primary and secondary aliphatic halides and halogen ions probably occurs by means of a Walden inversion.[1] The free halogen ion approaches the carbon atom which carries the organic halogen atom from the opposite direction following a line through the carbon atom and the organic halogen atom. Some experiments have been made to prove this theory by using aliphatic halides containing an asymmetric carbon atom. The differences between the rate of racemization and the rate of the exchange reactions were lower than 10% in these cases.[1]

Most of the experiments with organic halides have been carried out in organic solvents. The exchange reaction of α-bromopropionic acid and inorganic bromide has been investigated in aqueous acid solution by Koskoski, Dodson and Fowler.[2] They found a bimolecular reaction mechanism. The reaction was independent of the concentration of the sulfuric acid, which had been used to suppress the ionization of the acid.

In this paper the results of some exchange reactions of aliphatic iodides and inorganic iodide or iodine in aqueous solution are given.

The following reactions have been investigated (the labeled iodine atom is represented by I*)

	Reaction	Table
(A)	$CH_2ICOOH + I^{*-} \rightleftarrows CH_2I^*COOH + I^-$	I
(B)	$CH_2ICOO^- + I^{*-} \rightleftarrows CH_2I^*COO^- + I^-$	I
(C)	$CH_2ICOOH + I_2^* \rightleftarrows CH_2I^*COOH + I_2$	
(D)	$CH_2ICOOH + I_3^{*-} \rightleftarrows CH_2I^*COOH + I_3^-$	II
(E)	$CH_2ICOOCH_3 + I^{*-} \rightleftarrows CH_2I^*COOCH_3 + I^-$	I

Radioactive Iodine.—In all cases the inorganic fraction has been labeled with iodine-131. This isotope has a soft β-radiation and a γ-radiation with a half-life of 8.0 days. The amount of I^{131} has been determined by counting the β-rays with a Geiger–Müller counter. Throughout the investigation the activity of the iodine was measured on samples of silver iodide, sedimented on copper discs. The corrections for self absorption of these samples were determined with the graphic method.[3] As this

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[1] E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley and J. Weiss, *J. Chem. Soc.*, 1525 (1935); E. D. Hughes, F. Juliusberger, A. D. Scott, B. Topley and J. Weiss, *ibid.*, 1173 (1936); W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, 1252 (1937); W. A. Cowdrey, E. D. Hughes, T. P. Nevell and C. L. Wilson, *ibid.*, 209 (1938).

[2] W. K. Koskoski, R. W. Dodson and R. D. Fowler, THIS JOURNAL, **63**, 2149 (1941).

[3] A. H. W. Aten, Jr., *Nucleonics*, **6**, No. 2, 68 (1950); *Chem. Weekblad*, **47**, 554 (1951).