Kinetics of Iodine Exchange between Zinc Iodide and *n*-Propyl and *n*-Butyl Iodide in Acetonitrile

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The exchange of iodine between zinc iodide and *n*-propyl iodide and between zinc iodide and *n*-butyl iodide has been studied in the temperature range 40–59° and in the zinc iodide concentration range 5×10^{-4}–10^{-2} *M*. This exchange has been found to be first order with respect to *n*-propyl iodide or *n*-butyl iodide and zero order with respect to zinc iodide. The values of the Arrhenius parameters, E_a and log *A*, for *n*-propyl iodide are 22.6 ± 0.2 kcal/mol and 11.9 ± 0.3 (*A* in $\sec^{-1}$), respectively, and for *n*-butyl iodide these values are 19.4 ± 0.8 and 9.6 ± 0.2.

The following research provides a test of the commonly accepted generalization that S_N2 kinetics are to be expected for nucleophilic exchange reactions of primary alkyl halides whereas S_N1 kinetics are more probable for tertiary or secondary alkyl halide exchange. Acetonitrile was chosen for the solvent, and in it was dissolved the poor nucleophile zinc iodide along with a normal alkyl halide. The zinc iodide was labeled with iodine-131 in order that the exchange rate could be followed.

Determination of the exchange rate of iodine atoms between *n*-butyl iodide and zinc iodide in acetonitrile was previously made by Hodgson, Evans, and Winkler[2] by labeling these compounds with radioactive iodine. These investigators found the exchange to be first order with respect to each reactant. The zinc iodide order determination was made at 100° and was based on rate measurements made on two solutions with the same *n*-butyl iodide concentration but different concentrations of zinc iodide.

Experimental Section

Labeling of zinc iodide was done with carrier-free sodium iodide obtained from Oak Ridge National Laboratories. A 30-mCi sample of NaI^{131} in 2.0 ml of solution containing 0.2% cysteine hydrochloride was diluted to 20 ml with 0.001% sodium thiosulfate solution and 10 μCi was taken from this and rinsed with deionized water into a 25-ml volumetric flask, and the resulting solution was evaporated to dryness. The residue was dissolved in 25 ml of acetonitrile and 1.0–2.0-ml portions were withdrawn from this solution and used to label the zinc iodide.

The zinc iodide used was national formulary quality. It was dried for 1 hr in an electric oven at a temperature of 127°. The dried salt was stored in a desiccator until used.

The *n*-propyl iodide was Eastman Organic Chemical, white-label grade. If this material showed any yellow discoloration, it was shaken with mercury until the yellow color disappeared, and the clear, colorless liquid was used. A portion of this liquid was run through a gas chromatograph, and the results showed the presence of approximately 2% impurity with a boiling point, estimated from the chromatogram, to be 117–125°. The *n*-butyl iodide and isopropyl iodide were also Eastman Organic Chemical, White Label grade but were not chromatographed.

The acetonitrile was industrial grade and was supplied by Matheson Coleman and Bell Co. It was dried by shaking with anhydrous potassium carbonate, then filtered, and distilled. The fraction boiling at 81.4–81.6° (760 mm) was collected and used as solvent.

Stock solutions to be used to prepare exchange solutions were made by weighing the solute in a weighing bottle to the nearest tenth of a milligram. The solute was rinsed into a volumetric flask and diluted to the appropriate volume with acetonitrile. Exchange solutions were prepared by pipeting the required amount from the stock solutions and adding acetonitrile.

The zinc iodide stock solution so prepared was found to be turbid probably owing to the presence of small amounts of zinc oxide which failed to dissolve in acetonitrile. The solution was therefore filtered and standardized by titration with freshly prepared standard silver nitrate solution using eosin indicator. The silver nitrate in turn had been standardized by titration with a solution made from dried, weighed, reagent grade potassium chloride using potassium dichromate indicator.

Stock solutions to be used at 59.1° were swirled and swept for 5 min with nitrogen gas which was dried by passing it through concentrated sulfuric acid. After all reactants were mixed, the solution was swept for 3 min with nitrogen if it was to be used at 59.1°.

Exchange reactions were carried out in 25- or 50-ml volumetric flasks fitted with ground-glass stoppers which were lubricated with Fisher Cello-Seal. The flasks were placed in racks in a thermostat equipped with a stirrer, heating element, and a thermoregulator. The temperature of the water which filled the thermostat was constant within ±0.05°.

Samples were counted in a Picker Model 2804 Well-Type scintillation detector in conjunction with a Picker Model Number 5832 Spectroscaler II. The 364-keV γ radiation from I^{131} was counted.

Samples which were to undergo exchange were prepared by adding the required amounts of zinc iodide solution, tracer, and acetonitrile to a 25- or 50-ml volumetric flask. These reactants were allowed to equilibrate overnight. At the time the exchange reaction was begun, organic iodide solution was added to the volumetric flask. Time of mixing was taken as the time at which half the organic iodide had been added. The mixture was shaken 100 times if the exchange rate was to be measured below 50° or swirled with nitrogen if the exchange rate was to be measured above 50°. Comparison of the exchange rates of solutions run at 47.5° swept with nitrogen with those not swept with nitrogen showed that sweeping with nitrogen did not change the exchange rate at this temperature.

After the reactants were mixed, the volumetric flasks containing the individual samples were placed in the thermostat and 1.0-ml portions were withdrawn from each flask at appropriate time intervals. The milliliter portion was run into 1.0 ml of benzene which had been chilled in ice, and the resulting mixture was shaken vigorously 75 times and then centrifuged for 5 min. Most of the organic iodide dissolved in the benzene layer, and most of the zinc iodide dissolved in the water layer. Completeness of separation was measured by dissolving labeled zinc iodide in acetonitrile and shaking this solution with milliliter portions of benzene and water. In the water layer was found 95.3% of the activity. Comparison of the observed distributions of activities in solutions which had come close to equilibrium with those calculated from concentrations indicate that less than 1% of the *n*-alkyl iodide activity appears in the water layer.

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[1] This report is based on a portion of a thesis submitted by B. F. Howell in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Missouri, Aug 1964. It has been presented at the 16th Annual Midwest Chemistry Conference, Kansas City, Mo., Nov 1964.

[2] G. W. Hodgson, H. G. V. Evans, and C. A. Winkler, *Can. J. Chem.*, **29**, 60 (1951).

After centrifuging, the two layers were separated by withdrawing the water layer from under the benzene layer with a pipet and allowing the water layer to flow into another test tube of the same size. Water was added to the test tube containing the water layer until the volumes of the two solutions were equal. The samples were then counted. The minimum number of counts was 4000, and the minimum time of counting was 3 min.

The number of counts and the counting time were recorded for each water and benzene sample. Solutions from the same sample in the thermostat were always counted consecutively so that the error due to I^{131} decay was inappreciable.

Correction factors for the expansion of solvent with temperature were made for all concentrations reported.

Calculation of Results.—Counting rates for the water layer containing zinc iodide and the benzene layer containing propyl iodide were used to calculate the exchange rate, R, using eq 1[3]

$$R = \frac{ab(0.693)}{(a + b)t_{1/2}} \qquad (1)$$

in which a is the molar concentration of organic iodide in the sample, b is the concentration of zinc iodide in gram equivalent per liter, and $t_{1/2}$ is the time of half-exchange which is evaluated by plotting the logarithm of $(1 - f)$ as a function of time where f is the fraction of exchange which has occurred at a particular time.

Values of log R at constant values of b were plotted against log a to determine the reaction order with respect to n-propyl iodide and the value of the rate constant, k. The order with respect to zinc iodide was determined by plotting log R at constant values of a against log b.

Results

Representative results for order determinations using n-propyl iodide and zinc iodide appear in Table I, and a summary of the exchange results at various temperatures appears in Table II. Tables III and IV contain similar representative data obtained using n-butyl iodide.

TABLE I

ORDER DETERMINATIONS FOR IODIDE EXCHANGE BETWEEN n-PROPYL IODIDE AND LABELED ZINC IODIDE IN ACETONITRILE AT 40.0°

n-PrI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	$t_{1/2}$ (hr)	$R \times 10^4$ (mol l.$^{-1}$ hr^{-1})	$k \times 10^4$ [a] (hr^{-1})
0.981	0.00205	6.71	2.12	1.94
0.686	0.00513	28.9	1.22	1.66
0.490	0.00513	44.9	0.784	1.60
0.294	0.00513	70.4	0.496	1.68
0.981	0.0200	91.0	1.48	1.51
0.981	0.0159	86.3	1.26	1.28
0.981	0.0120	65.4	1.26	1.28
0.981	0.00991	65.9	1.03	1.05
0.981	0.00794	43.4	1.28	1.31
0.981	0.00598	28.1	1.46	1.49
0.981	0.00397	15.4	1.78	1.82

[a] Order for ZnI_2, 0.0; order for n-PrI, 1.09.

From these data it appears that the reaction is first order with respect to n-propyl iodide and that the order with respect to zinc iodide is zero or slightly negative. The rate constant, k, shown in Table I is calculated for an over-all first-order reaction. The activation energy for the n-propyl iodide–zinc iodide exchange, calculated by the method of least squares, has the value 22.6 kcal/mol with a standard deviation of 0.2, and the value of log A, the frequency factor in the logarithmic form of the Arrhenius equation is 11.9 (A is measured in sec^{-1}) with a standard deviation of 0.3.

TABLE II

SUMMARY OF EXCHANGE DATA FOR n-PROPYL IODIDE AND ZINC IODIDE

Temp (°C)	n-PrI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	No. of trials	$k \times 10^4$ (hr^{-1})	σ_k
40.0	0.981–0.0490	0.0200–0.00115	14	1.5	0.2
47.5	0.968–0.387	0.0200–0.00489	14	3.0	0.1
50.0	0.725–0.0967	0.0928–0.00769	14	5.2	0.1
59.1	0.954–0.191	0.0385–0.00100	7	13.0	0.6

TABLE III

ORDER DETERMINATIONS FOR IODIDE EXCHANGE BETWEEN n-BUTYL IODIDE AND LABELED ZINC IODIDE IN ACETONITRILE AT 40.0°

n-BuI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	$t_{1/2}$ (hr)	$R \times 10^4$ (mol l.$^{-1}$)	$k \times 10^4$ [a] (hr^{-1})
0.964	0.00811	63.6	0.876	0.909
0.771	0.00811	58.7	0.977	1.27
0.578	0.00811	77.5	0.715	1.24
0.385	0.00811	153	0.359	0.931
0.964	0.00609	50.2	0.836	0.867
0.964	0.00406	28.3	0.989	1.03
0.964	0.00304	19.4	1.08	1.12

[a] Order for ZnI_2, 0.0; order for n-BuI, 0.9. Average $k = (1.1 \pm 0.2) \times 10^{-4}$.

TABLE IV

SUMMARY OF EXCHANGE DATA FOR n-BUTYL IODIDE AND ZINC IODIDE

Temp (°C)	n-BuI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	No. of trials	$k \times 10^4$ (hr^{-1})	σ_k
40.0	0.964–0.385	0.00811–0.00304	7	1.1	0.2
47.5	0.467–0.0953	0.0930–0.0281	8	2.9	0.2
60.0	0.902–0.181	0.00497–0.00199	12	7.3	1.2

It may be seen from Tables III and IV that results for n-butyl iodide and n-propyl iodide are similar; the order for n-butyl iodide is also one, and that for zinc iodide is once again zero within the limits of experimental error. Rate constants are smaller for n-butyl iodide as would be predicted from a consideration of ponderal effects. The activation energy is 19.4 ± 0.8 kcal/mol and log A is 9.6 ± 0.2 where A is expressed in reciprocal seconds.

Exchange experiments with zinc iodide were also performed with isopropyl iodide. It was not possible to obtain precise results with this substance since log $(1 - f)$ against time plots were found to be curved, possibly because of gradual dehydrohalogenation of the isopropyl iodide. This process is indicated by the appearance of a yellow color in the solutions with the passage of time. The yellow color was found spectrophotometrically to be due to the presence of iodine which could form readily from hydrogen iodide under the existing reaction conditions. The experimental results did, however, show that exchange is much slower with isopropyl iodide than with comparable solutions of n-propyl iodide at the same temperature. Time of half-exchange in n-propyl iodide is 51.2 hr, whereas in isopropyl iodide it is 226 hr. This sort of result was observed in approximately 50 trials made with isopropyl iodide. Secondly, exchange with isopropyl iodide appears also to be zero order with respect to zinc iodide. This fact is indicated by comparing the

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[3] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1951.

result obtained in six trials involving exchange between zinc iodide having concentrations ranging from 1.11 to 8.89 × 10^{-4} N and 1 M isopropyl iodide with those employing 0.7–3.5 × 10^{-2} N zinc iodide and 1 M isopropyl iodide. The time of half-exchange using the more dilute zinc iodide is much less than that using the more concentrated zinc iodide, characteristic behavior for a zero-order reactant.

Attempts were made to evaluate the effects of various impurities on the reaction order for zinc iodide. When 80 λ's of water was added to various concentrations of zinc iodide solutions, while the propyl iodide concentration was held constant, it was observed that water accelerated the reaction at small concentrations of zinc iodide but that the effect was not significant above concentrations of 10^{-2} N. Results of this study appear in Table V. Additional experiments showed that addition of much larger amounts of water does not result in a further rate increase.

TABLE V

THE EFFECT OF ADDED WATER ON THE EXCHANGE RATE

Run no.	Temp (°C)	n-PrI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	H_2O (mol l.$^{-1}$)	$R \times 10^4$ (mol l.$^{-1}$ hr^{-1})
49-3	59.1	0.954	0.0118	0.424	19.6
49-4	59.1	0.954	0.00884	0.424	19.8
49-5	59.1	0.954	0.00600	0.424	22.0
49-6	59.1	0.954	0.00295	0.424	28.5
49-7	59.1	0.954	0.00997	0.424	76.4

The exchange rate of n-propyl iodide with a solution containing only the carrier-free sodium iodide was measured. The amount of tracer customarily used to label the zinc iodide solution produced a solution which was approximately 3 × 10^{-16} M sodium iodide. When exchange was allowed to occur between the tracer and 2 M n-propyl iodide it was 95% complete in 20 min which indicates that the iodide ion as such was not present during zinc iodide exchange because zinc iodide exchange takes place much more slowly.

Free iodine was added to acetonitrile solutions of labeled zinc iodide and unlabeled n-propyl iodide, and the exchange rate was measured in an attempt to evaluate the effect of iodine. The rate of this exchange was measured by separating the iodine and the zinc iodide from n-propyl iodide with an 0.1 M water solution of sodium thiosulfate. The rate of this exchange was nearly the same as the rate of exchange of n-propyl iodide and iodine alone and only about one-fourth as fast as the exchange between zinc iodide and propyl iodide alone. Results appear in Table VI.

TABLE VI

EXCHANGE RATES IN THE PRESENCE OF IODINE

Temp (°C)	n-PrI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	I_2 (mol l.$^{-1}$)	$t_{1/2}$ (hr)	$R \times 10^4$ (mol l.$^{-1}$ hr^{-1})
59.1	0.954	0.00590	0.00110	18.4	3.01
59.1	0.954	0	0.00110	4.29	3.58
59.1	0.954	0.00199	0	0.995	13.8

Exchange rates were also measured for zinc iodide and n-propyl iodide in the presence of added iodide ion. Enough iodide ion was added, in the form of potassium iodide, on a mole to mole basis to react with the zinc iodide to produce what was presumed to be ZnI_3^-, a complex which is known to exist in water solution[4] and in N,N-dimethylformamide.[5] The reaction order was determined by using equimolar amounts of ZnI_2 and I^- in varying concentrations while holding the n-propyl iodide concentration constant. The rate was found to be slower than that of iodide ion alone, but faster than that of zinc iodide. The order with respect to ZnI_3^- was found to be approximately one-third, and exchange in this system is probably by means of iodide ion. Data appear in Table VII. These results suggest that ZnI_3^- is not involved in the rate-determining step of the zinc iodide–n-propyl iodide exchange even when equimolar quantities of zinc iodide and potassium iodide are used.

TABLE VII

THE EFFECT OF ADDED IODIDE ON THE EXCHANGE RATE

Temp (°C)	n-PrI (mol l.$^{-1}$)	ZnI_2 (equiv l.$^{-1}$)	Added I^- (mol l.$^{-1}$)	$t_{1/2}$ (hr)	$R \times 10^4$ (mol l.$^{-1}$ hr^{-1})
42.5	0.763	0.0119	0.00537	0.818	1.43
42.5	0.763	0.00848	0.00384	0.630	1.34
42.5	0.763	0.00678	0.00307	0.546	1.24
42.5	0.763	0.00509	0.00230	0.437	1.13
42.5	0.763	0.00339	0.00153	0.323	1.05
42.5	0.763	0.00170	0.000767	0.202	0.843

Discussion

Comparison of preliminary exchange results between sodium iodide and n-propyl iodide with results obtained by Thuillier and Daudel[6] gave reasonably good agreement. Both sets of results showed the exchange to be first order in each reactant.

As mentioned previously Hodgson, *et al.*, have measured exchange rates between zinc iodide and n-butyl iodide in acetonitrile and have found first-order dependence on both reactants at 100°.[2] The rate constant reported by these investigators at 47.5° is 6.0 × 10^{-3} l. mol^{-1} hr^{-1} which, if calculated assuming zero-order dependence upon zinc iodide, becomes 2.88 × 10^{-4} hr^{-1} and is seen to agree well with the value 2.9 × 10^{-4} hr^{-1} obtained by the authors. On the basis of their observation that the apparent degree of ionization of zinc iodide does not change with changing zinc iodide concentrations, the Canadians conclude that simple iodide ion is not the main reacting species. The authors agree with this conclusion since exchange by simple iodide ion produces one-third-order dependence upon zinc iodide concentration for complete ionization

$$ZnI_2 \longrightarrow Zn^{2+} + 2I^- \qquad (2)$$

and one-half-order dependence for incomplete ionization of zinc iodide.[7] The Canadian chemists conclude

$$ZnI_2 \longrightarrow ZnI^+ + I^- \qquad (3)$$

that either undissociated molecules (ion pairs) of zinc iodide are involved in the exchange or else exchange is

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(4) F. Albert Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p 477.

(5) R. L. Beyer, Ed.S. Thesis, Kansas State Teachers College, Aug 1967.

(6) G. Thuillier and P. Daudel, *Compt. Rend.*, **243**, 147 (1956).

(7) J. Minor, M.S. Thesis, Kansas State Teachers College, Aug 1967.

by means of a complex ion such as ZnI_3^- produced by the following reaction. Therefore, if the reaction order

$$2ZnI_2 \longrightarrow ZnI_3^- + ZnI^+ \tag{4}$$

for zinc iodide at 100° is indeed one, the reaction proceeds by different mechanisms at 100° and 40–60°.

In calculating results for exchange rates, corrections for the 4.7% zinc iodide activity in the organic layer and the <1% *n*-alkyl iodide activity in the inorganic layer were not made by the authors because the measured exchange proceeded to within 99% of the theoretical value in cases where it was followed this long. If the amounts of zinc iodide and alkyl iodide going into the benzene and water layers, respectively, were seriously biasing the results, the theoretical and observed values for the amount of exchange at equilibrium would not be within 1% of each other.[8]

It was found that exchange reactions performed with zinc iodide and *n*-propyl iodide at 59.1° gave erratic results and showed a pronounced rate increase with the passage of time when run in the presence of atmospheric oxygen. Therefore studies made at this temperature were done using solutions swept with nitrogen.

A mechanism which is consistent with the first-order rate dependence observed for *n*-propyl iodide and zero-order dependence observed for zinc iodide is one in which a solvent molecule approaches the iodine-containing carbon atom from the side opposite the iodine and produces an ion pair. The formation of these complexes is proposed as the rate-determining step. A weakening of the carbon–iodine bond is indicated since the activation energy is only 22.9 kcal/mol for *n*-propyl iodide whereas the bond strength is 46 kcal/mol.[9] Solvent assistance in the bond-breaking step is assumed to occur since *n*-propyl iodide undergoes exchange with zinc iodide many times faster than does isopropyl iodide, contrary to what would be expected for unimolecular decomposition of alkyl iodides. This result would be expected if solvent assistance is involved since the carbon-containing iodine in isopropyl iodide is more sterically hindered.

Zinc iodide probably exists primarily as undissociated molecules in acetonitrile.[2] Since zinc iodide is a Lewis acid it can easily attach itself to the iodide ion in the ion pair and either give an iodide ion to the propyl group at the same time or shortly thereafter.

$$CH_3C{\equiv}N{:} + R{-}I \overset{k}{\rightleftharpoons} [CH_3\overset{+}{C}{=}N{:}R \longleftrightarrow CH_3C{\equiv}\overset{+}{N}{:}R]I^- \tag{5, rate determining}$$

$$[CH_3C{\equiv}N{:}R]^+I^- + I^*ZnI \longrightarrow CH_3C{\equiv}N + RI^* + ZnI_2 \tag{6}$$

Although this mechanism is consistent with experimental observations reported in this paper, the possibility of other mechanistic explanation is, of course, not precluded.

The proposed mechanism assumes that the reaction is in reality bimolecular: first order in alkyl iodide and first order in acetonitrile. A further indication of bimolecularity in the rate-determining step is the value of the Arrhenius frequency factor, $10^{11.9}$ l. mol^{-1} sec^{-1}. This is very close to the value, 10^{11}–10^{12} l. mol^{-1} sec^{-1},[10] calculated from collision theory for a bimolecular reaction, whereas the value for a unimolecular reaction is 10^{13}–10^{14} sec^{-1}.

At first glance, the results of this study appear to violate the usual rules governing SN1 and SN2 reactivity of alkyl halides. However, if a solvent molecule is regarded as making a nucleophilic attack on the alkyl halide molecule in the rate-determining step, then the observed results agree with results of other investigators who have studied SN1 and SN2 reactivities.

Registery No.—Iodine, 7553-56-2; zinc iodide, 10139-47-6; *n*-propyl iodide, 107-08-4; *n*-butyl iodide, 542-69-8; acetonitrile, 75-05-8.

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(8) This point has been adequately verified in the author's laboratory in working with systems involving labeled zinc iodide, *n*-butyl iodide, and N,N-dimethylformamide. Incomplete separation of the organic and inorganic iodides has lead to experimental equilibrium values which were off as much as 70% from the theoretical equilibrium values.

(9) S. Glasstone and D. Lewis, "Elements of Physical Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1960, p 92, taken from Szwarc, *Quart. Rev.* (London), **5**, 22 (1951).

(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1961, p 75.