EXCHANGE OF RADIOIODINE
BETWEEN INORGANIC AND ORGANIC IODIDES

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by

Gordon Wesley Hodgson M.Sc.

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A KINETIC STUDY OF THE
EXCHANGE OF RADIOIODINE BETWEEN
n-BUTYL IODIDE AND SOME INORGANIC IODIDES

- INTRODUCTION -

In an exchange reaction two compounds having one atom in common are mixed and an interchange of the common atom takes place between the two compounds. The extent of the exchange is measured by making the common atom in one of the compounds detectable as a radioactive or stable isotope, the former being preferred because it is more readily traced. At the end of the reaction time the two compounds are separated and the distribution of the isotope measured. If complete exchange has taken place each compound has the same proportion of isotope, but if no exchange has occurred all the isotope is found in the original compound.

The exchange reaction has been recognized as a valuable tool in chemistry, particularly in organic chemistry, because it gives direct information regarding bond reactivities and reaction mechanisms. The reaction offers an excellent method of studying some of the most fundamental properties of chemical compounds because it provides a remarkably simple system. Since the reactants and products are chemically identical there is no heat of reaction, only an energy of activation; concentrations remain constant and there are no interfering products or by-products.

It is, therefore, somewhat surprising to note that the mechanism of the exchange reaction in solution has not been completely studied. When an inorganic halide is mixed with an organic halide an exchange may take place but it has not been established in all cases whether reaction occurs between the organic molecule and the inorganic molecule, or whether it involves halide ion resulting from ionization of either the inorganic molecule or the organic halide. Conceivably more than one of these mechanisms is concerned.

Since the exchanges between inorganic halides and halogens, which takes place readily in solution (1, 2, 3, 4, 5), are almost certainly ionic reactions, the ionic mechanism has been assumed for similar reactions in non-aqueous solutions. It has been generally assumed, too, that the ionic mechanism holds for exchanges of organic halides with inorganic halides in non-aqueous solutions.

At first it was reported that organic halides do not exchange with inorganic halides (4, 7) but later workers showed that alkyl halides do undergo thermal exchange at elevated temperatures (6, 8). Much of the early work, as reviewed by Seaborg (9) and Haissinsky and Daudel (10), was of a qualitative nature in which the attempted exchanges were reported as being very rapid, slow, or "no exchange", the object of the investigations being to obtain rough estimates of the reactivity of the various organic halides. The qualitative nature of much of the work was compelled by the fact that the isotopes available at the time were too short-lived to permit precise kinetic studies. The iodine isotope was I^{128} with a half-life of about twenty-four minutes, and the bromine tracer was a mixture of isotopes having a half-life of about thirty hours.

The first attempt to determine the reaction mechanism for the exchange of inorganic halides with organic halides in non-aqueous solution was made by McKay (11). From the observation that the exchange of methyl iodide with sodium iodide in ethanol took place much more readily than the exchange of the organic iodide with iodine, it was concluded that the mechanism for the exchange was a reaction of the organic iodide with the iodide ion. This conclusion was supported by the fact that the presence of a solvent accelerated the exchange of a halogen between inorganic and organic halides (6).

When kinetic studies of exchange reactions began to be made, no rigorous investigation into the mechanism of the reaction was made, and the ionic mechanism was tacitly assumed. Thus, Seelig and Hull (12) based their study of the exchange of sodium iodide with various aliphatic iodides on the ionic mechanism because it was believed that an earlier investigation had shown the exchange between aliphatic iodides and iodide ion to be possible (13). In the earlier investigation however, no attempt had been made to prove the mechanism; the assumption was made that since the exchange between iodide and sodium iodide was obviously an ionic reaction the reaction between sodium iodide and an organic iodide in a non-aqueous solution was therefore an ionic reaction.

A similar assumption was made by Sugden and his co-workers in investigations of the exchange of bromine between lithium bromide and various aliphatic bromides (14, 15, 16).

In an attempt to elucidate the mechanism of the racemization of d-sec.-octyl iodide by sodium iodide a study of the exchange reaction between the two compounds was made (17). The interchange was found to occur at almost the same rate, when expressed in the correct units, as the racemization. It was inferred that the steriochemical inversion of the organic iodide involves an exchange between iodide ions in solution and the iodine atom of the octyl iodide. It was concluded that the exchange takes place through a Walden inversion in which the exchanging ion approaches the carbon atom carrying the halogen and attaches itself to the weak face-centred bond opposite the halogen atom. As the attacking ion approaches the centre of the carbon atom the other halogen atom recedes until it is quite separate from the organic molecule.

While the results undoubtedly showed that the mechanism of the inversion was the same as that of the exchange, the ionic mechanism was not proven to be the true mechanism. That is, the exchange and inversion could have been accomplished by the interaction of an organic iodide molecule with an undissociated inorganic molecule.

A somewhat different view was taken by Fairbrother who exchanged various bromides with a number of inorganic bromides (18). Although his investigations were not precise kinetic studies he found that all organic bromides exchanged readily with aluminum bromide, and less readily with tin and antimony bromides. Zinc and mercuric bromides were less active and it was found that potassium bromide did not exchange under the same experimental conditions. If the ionic mechanism were the one and only mechanism for exchange, the above order of reactivity should have been reversed, because the degree of ionization of the inorganic iodides decreases from potassium bromide to the other bromides. Clearly, the ionic mechanism is not the only mechanism for the exchange of a halogen between inorganic and organic halides.

There is additional evidence to show that the reaction of organic halides with alkali halides is quite different from the reaction with aluminum halides. Roginsky and his co-workers (19) made a kinetic study of the exchange between ethyl bromide and aluminum bromide and found an activation energy of 11.2 kcal. per mole for the reaction, while the activation energy for the alkali halide reactions has been found to be approximately 20 kcal. (12, 16, 20). Fairbrother (21), investigating the mechanism of the Friedel-Crafts reaction concluded that aluminum halides exchange with aliphatic halides by forming tetrahalide complexes. Thus exchange through an ionization of the carbon halogen bond of the organic halide was postulated.

This view was supported to some extent by the results of exchange experiments involving the reactions between gaseous methyl bromide and solid aluminum, barium, and potassium bromides (22). The activation energy for the aluminum halide exchange was only about 4.6 kcal., while that for the barium bromide exchange was found to be about 12 kcal.; no reaction was found to take place with potassium bromide.

The mechanism for the exchange of organic halides with elemental halogens is also a point of interest. From the study of the exchange of iodine with cis- and trans-diiodoethylene (23) it was concluded that the mechanism for the reaction involved the interaction of the organic iodide with iodine atoms. This conclusion was drawn from the observation that the order of the reaction was 1.5, the rate being dependent on the square root of the iodine concentration and the first power of the organic iodide concentration. Studied in both hexane and decalin, the exchange took place both thermally and photochemically. It was claimed that the presence of the double bond was essential for the exchange reaction because the atoms reacted with the electrons of the double bond.

No double bond was necessary for the exchange of bromine with trichlorobromomethane. Studied independently by two groups of workers (24, 25) the reaction appeared to be atomic in carbon tetrachloride solution, in the liquid phase, and in the gas phase. The order of the reaction was 1.5, the rate depending on the square root of the concentration of bromine.

The activation energies for the two foregoing halogen exchanges also suggested that the mechanism of the exchange was quite different from that of inorganic halide exchanges, for the former have relatively high activation energies of the order of 30 kcal. per mole while the latter have energy barriers of about 20 kcal. An exception appears to be the exchange of bromine with carbon tetrabromide (26) which is characterized by an activation energy of only 3 kcal. in the liquid phase and approximately zero in the gas phase. However, it was shown as before that the reaction involved halogen atoms.

It is significant that all the exchanges of elemental halogens which have been studied kinetically have been in the gas phase, liquid phase, or in a non-polar solvent where the atomic mechanism would be favored. No report has been made of kinetic studies of elemental halogen exchange in polar solvents where other mechanisms might be operative, such as the formation of a trihalide activated complex, or the formation of halide ions in the interaction between the halogen and polar solvent.

If the exchange of halides in solution is an ionic reaction it is reasonable to conclude that the nature of the solvent should have a marked effect on the rate of exchange, because the concentration of the halide ions would be a function of the ionizing power of the solvent. The only solvent studies made were those of Sugden and his co-workers (14, 15, 16) who studied the exchange of a series of aliphatic bromides with lithium bromide. In the solvents ethylene glycol diacetate, acetone, and a 90% acetone-water mixture, the relative rates for the exchange of butyl bromide were 1 : 100 : 18 for the three solvents respectively. Although the presence of water in the acetone should have increased the ionization of the lithium bromide, if that were possible, and consequently should have increased the exchange rate if the reaction were ionic, an increase in rate was not observed. In fact, the presence of the small quantity of water retarded the reaction. Hence solvent studies do little to clarify the mechanism of the exchange of organic halides with inorganic halides.

A more direct method of determining the mechanism of exchange with organic halides, would appear to be a study of the exchange of several inorganic halides with the organic halide in one solvent. If the reaction is strictly ionic in nature the absolute rate of exchange should be related directly to the degree of ionization of the inorganic halide. If, however, the mechanism included interaction of the inorganic halide molecules a direct relation with the degree of ionization of the inorganic halide should not exist. On the other hand, exchange between molecules having covalent bonds might be expected in the reaction of the organic halide with the elemental halogen since the bond in a halogen molecule is certainly more covalent than the halogen bond in most inorganic halides.

- EXPERIMENTAL and RESULTS -

The choice of the halogen was dictated by the availability and half-life of the radioactive isotope. I^{131} was readily available and its half-life of eight days was long enough to make its use as a tracer quite feasible. The half-life was short enough, however, that the health hazard associated with it was small, since a large accumulation of radioactive contamination in the laboratory was almost impossible. A simple calculation shows that if radioiodine were introduced into the laboratory at the rate of 0.5 mc. per month the radioactive content of the laboratory would at no time exceed 0.54 mc. and yet there would always be enough tracer available for the kinetic studies.

Normal butyl iodide was selected as the organic iodide. It was chosen instead of methyl or propyl iodides because of its higher boiling point (130°C). A higher boiling point implies a lower vapor pressure at ordinary temperatures, so that not only was it more convenient to handle, but as a radioactive compound it was safer to handle.

Inorganic iodides with electrostatic bonds were selected from the iodides of the alkali metals. To obtain reasonably complete information on the alkali iodides three members of the series were chosen, namely lithium, sodium, and caesium iodides, all of which may be regarded as completely dissociated in aqueous solution.

The other iodides used, in which the bonds have considerable covalent character, were zinc and cadmium iodides. Both compounds are virtually non-ionized in aqueous solution.

Acetonitrile was chosen as a solvent for the reactions. Apart from the fact that both the organic and inorganic halides could be dissolved in it to suitable concentrations, its relatively high dielectric constant appeared favourable for promoting ionization of the inorganic halide. The assumption was made at the outset that the relative, though perhaps not the absolute, extents of ionization of the inorganic halides would be the same in aqueous and acetonitrile solutions.

- Molecular Weight Determinations -

Molecular weight determinations were made to determine the relative degrees of ionization of the alkali iodides and zinc and cadmium iodides in acetonitrile solution.

The ebullioscopic method was used to determine the molecular weights, the calculations being made with the aid of the usual formula. Since the capacity of the apparatus was 50 ml. of acetonitrile (density 0.783 gm./ml. at 25°C) the apparent molecular weight was given by

$$M = \frac{1000 \times 1.3 \times G}{50 \times 0.783 \times \Delta t}$$

where Δt was the elevation of the boiling point caused by the addition of G grams of solute.

The standard Cottrell apparatus with an electrical heater and Beckman thermometer was used. Little or no superheating was observed in the determinations. Temperatures were determined within 0.002°, little or no solvent was lost during a determination, and weighings were accurate within 0.1%.

To obtain a relation between apparent molecular weight and concentration, successive additions of the solute to the boiling solution were made. Since considerable time was required for the solution of the salt after each addition a series of determinations extended over at least an hour during which time the barometric pressure could change appreciably. Such changes were noted and corrections based on both experimental observations and a calculation from the Clausius-Clapeyron equation were applied to the observed boiling point. The correction was 0.0044° per 0.1 mm. change in pressure. Since the molal boiling point elevation for acetonitrile is low, 1.3°, the pressure correction was important. For example, the addition of one gram of zinc iodide to 50 ml. of acetonitrile gave an elevation of 0.104°C. Thus a change in pressure of 0.1 mm., which could not be accurately observed, would give rise to a change in apparent molecular weight of four percent.

Fig. 1 shows the results of molecular weight measurements with sodium iodide and lithium iodide. The apparent molecular weight of caesium iodide was not determined because of its low solubility in acetonitrile. It is clear that the alkali iodides behave as strong electrolytes in acetonitrile, since the apparent molecular weights at infinite dilution are one half the true molecular weights, indicating that the molecules had dissociated into two ions.

Zinc iodide is not appreciably ionized in acetonitrile as indicated by the apparent molecular weights shown in Fig. 2. Fig. 2 also shows that not only is cadmium iodide not appreciably ionized in acetonitrile, but it apparently is slightly associated.

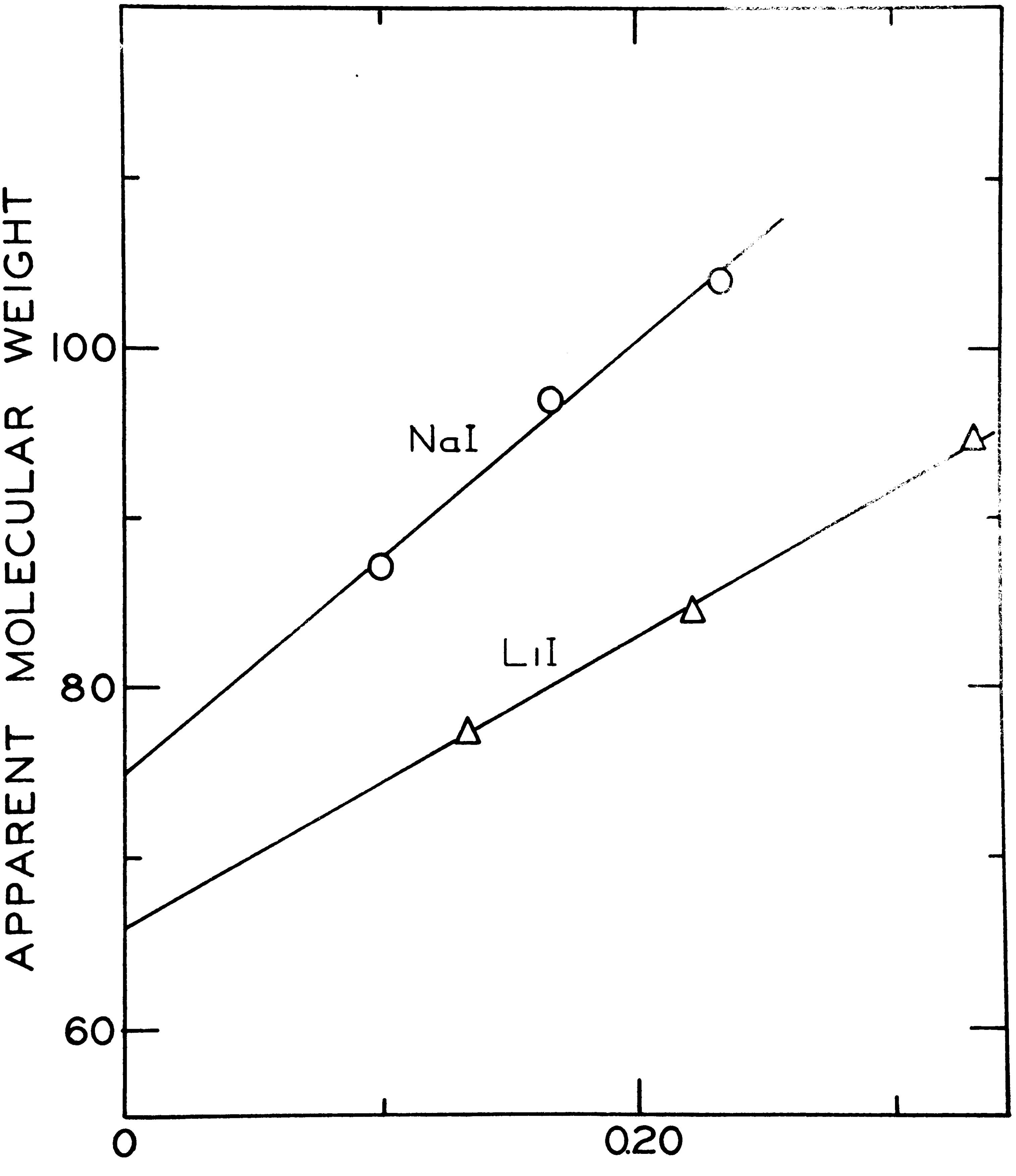

Fig. 1. Sodium iodide and lithium iodide molecular weight determinations.

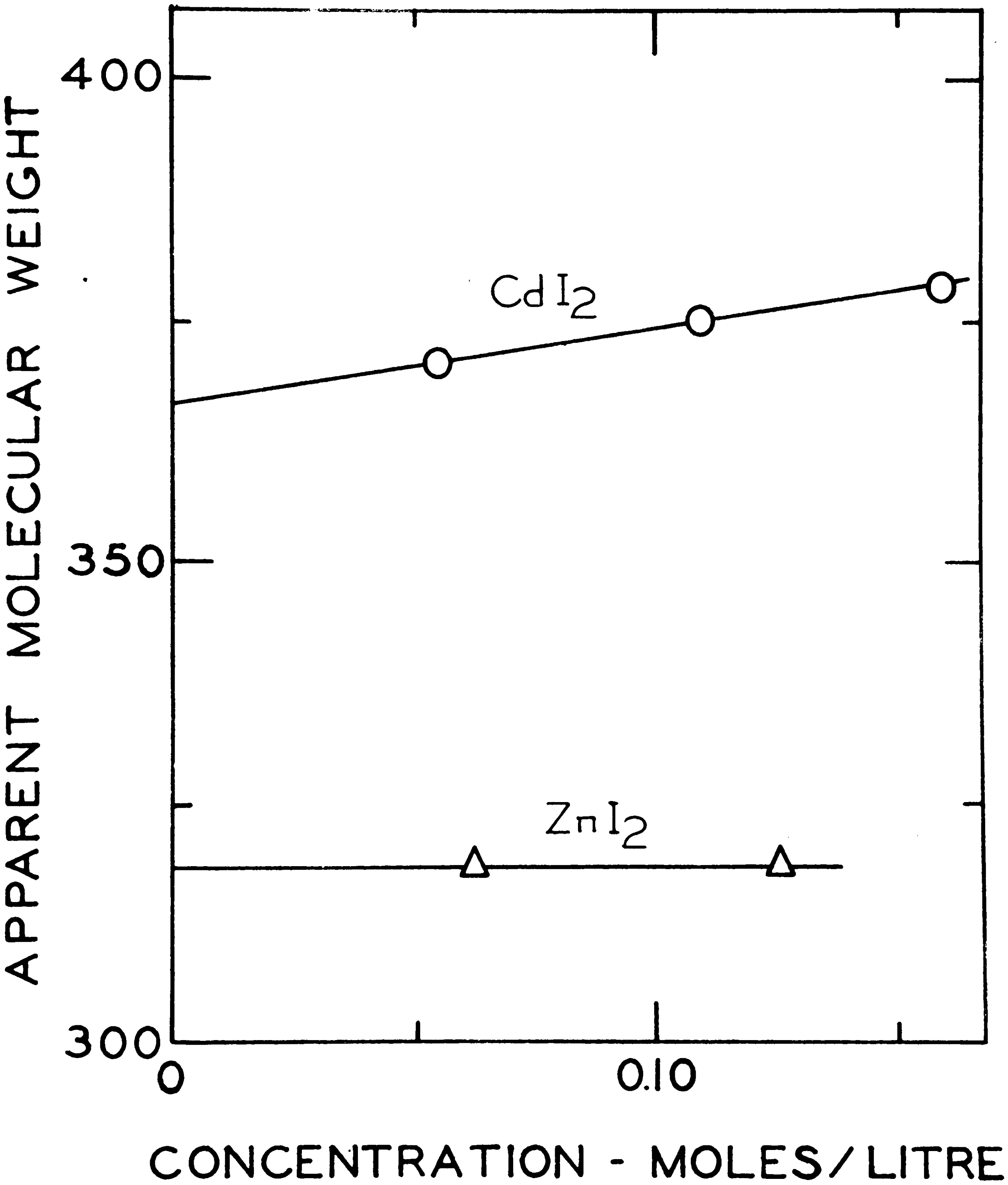

Fig. 2. Cadmium iodide and zinc iodide molecular weight determinations.

- Conductance Experiments -

The conclusions drawn from the molecular weight determinations were confirmed by conductance measurements.

Conductance data were obtained with a conductivity bridge Model RC-1 (portable) made by Industrial Instruments Inc. The conductivity cell was designed for use with solutions having high resistances, the cell constant being 45.6 as determined from measurements made on aqueous 0.02 M potassium chloride. All measurements were made at 25°C and corrections were applied for the specific conductance of the solvent. The specific conductance of acetonitrile was found to be 5 x 10^{-4} ohm^{-1}, indicating that the solvent was not completely dry, since the conductance of rigorously purified and dried acetonitrile is about 10^{-7} ohm^{-1} (29). The solvent, however, was the same as that used in the exchange experiments.

A plot of molar conductance against square root of the concentration of the iodide gave a straight line for each of the alkali iodides, as shown in fig. 3. This shows that the three alkali iodides behaved as strong electrolytes in acetonitrile solution.

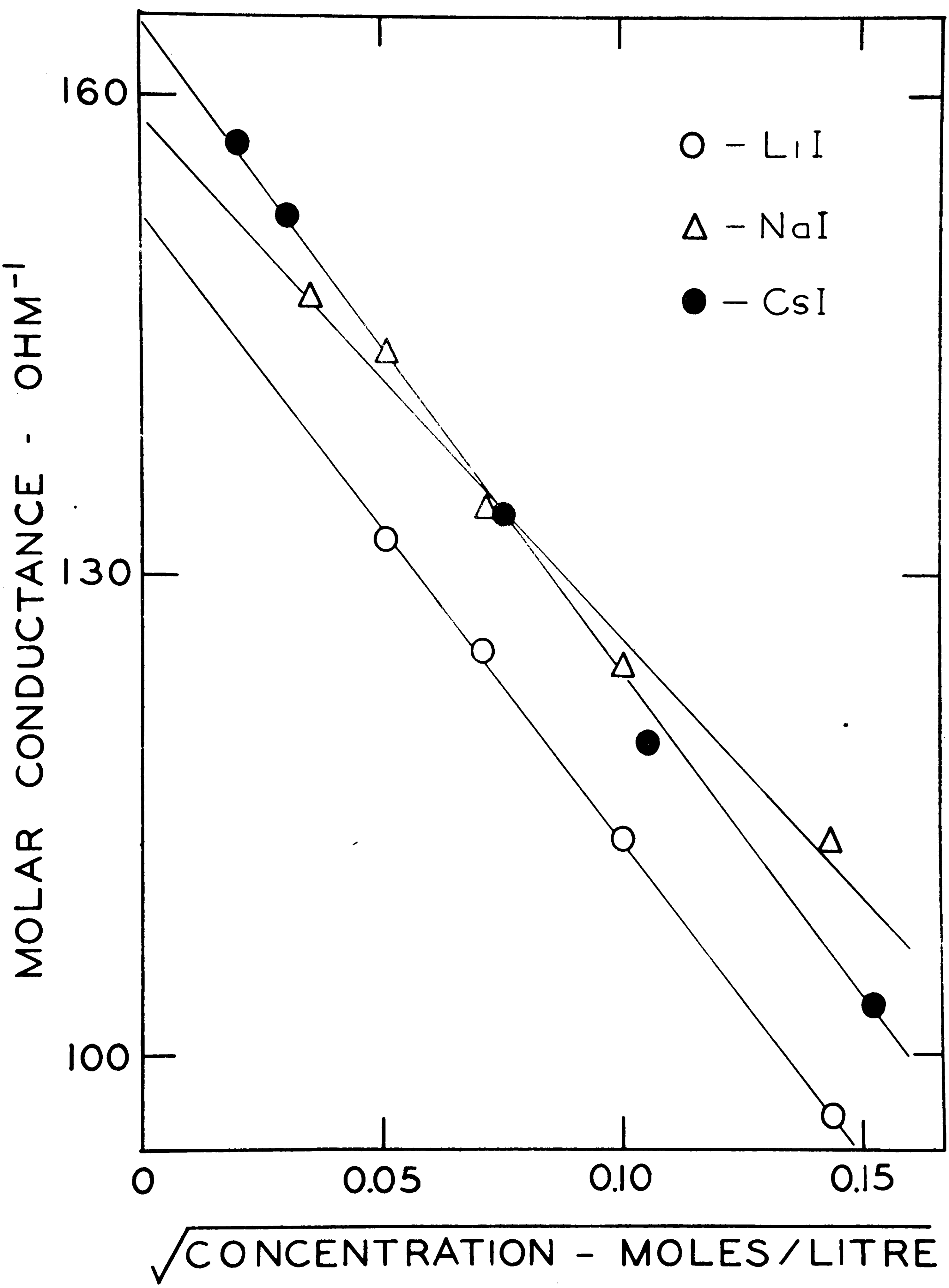

Fig. 3. Conductance of alkali iodides.

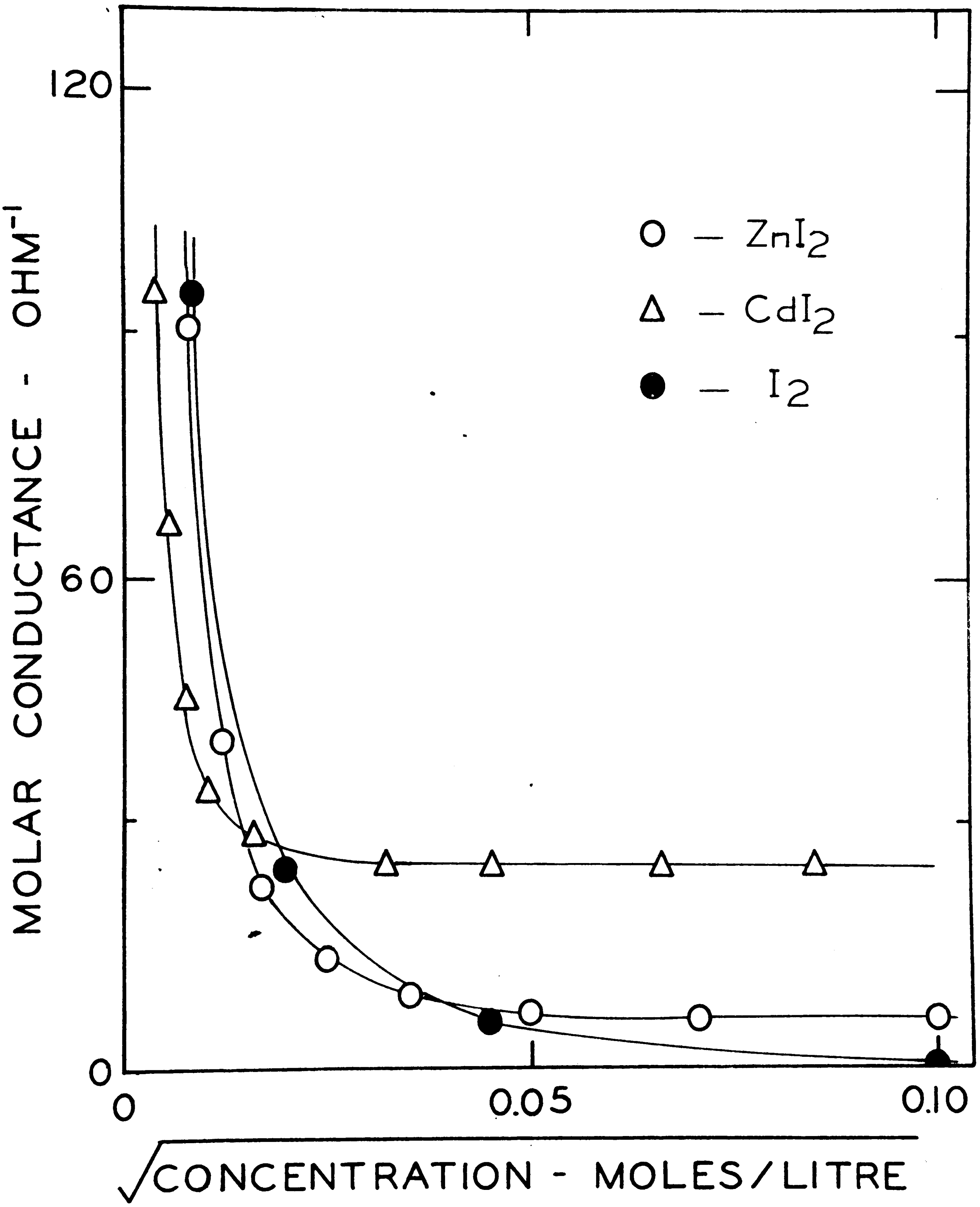

Fig. 4. Conductance of zinc iodide, cadmium iodide, and iodine.

Fig. 4 shows that zinc and cadmium iodides are weak electrolytes in acetonitrile solution. An estimate of the dissociation constant for the two iodides was made assuming the following simple ionization reactions:

$$ZnI_2 \rightleftharpoons ZnI^+ + I^-$$

$$CdI_2 \rightleftharpoons CdI^+ + I^-$$

From Ostwald's dilution law the dissociation constant is given by

$$K = \frac{\alpha^2}{1 - \alpha} C$$

where α is the degree of ionization and C is the concentration of the iodide. Conductance data give a measure of α as the ratio of the observed molar conductance to the molar conductance at infinite dilution. However, the conductance at infinite dilution of the system $ZnI^+ - I^-$ cannot be found readily because of the secondary ionization of the ZnI^+ ion. A reasonably good estimate can be made from the fact that the molar conductance is the sum of the ion conductances. The ion conductance of the iodide ion in acetonitrile is 101 ohm^{-1} (30) and the ion conductance for ZnI^+ and CdI^+ can be estimated since the ion conductances of most cations lie within a fairly narrow range. This is shown in Table I by some typical data from the literature (31) for aqueous solutions, and data in acetonitrile solution obtained from extrapolation of the conductance curves in fig. 3. The data in Table I indicates that the ion conductance of the ZnI^+ and CdI^+ ions are probably in the range 50 to 100 ohm^{-1}. The higher figure was assumed because the data in the table indicated that a higher conductance was associated with a larger cation. Hence, by adding the ion conductance of the iodide ion to the value assumed for each of the cations, the molecular conductance at infinite dilution for the two iodides was taken to be about 200 ohm^{-1}.

Table I. Ion conductances at infinite dilution at 25 C.

Ion	Weight	Ion Conductance, ohm^{-1} H_2O solution	Ion Conductance, ohm^{-1} CH_3CN solution
Li^+	6.9	37.3	57
Na^+	23.0	50.5	60
$\frac{1}{2}Ba^{++}$	68.7	64.2	
$\frac{1}{2}Pb^{++}$	103.4	71.4	
Ag^+	106.9	62.5	
Cs^+	132.9	77.5	66

The order of the dissociation constant calculated from the observed conductance and the conductance at infinite dilution is not changed even by large changes in the value assumed for the latter quantity. This is shown in Table II by calculations of the dissociation constant for zinc iodide based on the observed conductance of 10.5 ohm^{-1} at a concentration of 0.001 molar.

Table II. The relation between dissociation constant and the value assumed for the conductance at infinite dilution for zinc iodide.

Conductance at infinite dilution ohm^{-1}	Dissociation constant
150	4.9×10^{-6}
200	2.8×10^{-6}
250	1.8×10^{-6}

Table III shows the dissociation constants at various concentrations calculated from the conductivity data for cadmium iodide. It is apparent that the assumptions made in the Ostwald equation were not valid for these solutions since the values calculated for the constant were not constant over the entire concentration range. Nevertheless, a good indication of the degree of ionization is given.

Table III. The dissociation constant for cadmium iodide.

Concentration moles/litre	Molar conductance ohm^{-1}	Dissociation constant
0.0625	20.9	6.2×10^{-4}
0.0156	21.7	1.6
0.0040	22.0	4.0×10^{-5}
0.0010	22.6	1.2
0.00025	22.9	3.0×10^{-6}
0.0000625	37.7	2.7
0.0000312	49.1	2.5
0.0000156	66.4	2.5
0.0000078	81.8	2.2

The variation with concentration in the dissociation constants calculated for zinc iodide is comparatively little, as shown by the values in Table IV.

Table IV. The dissociation constant for zinc iodide.

Concentration moles/litre	Molar conductance ohm^{-1}	Dissociation constant
0.040	2.6	7.8×10^{-6}
0.020	2.6	3.9
0.010	2.6	2.0
0.005	5.6	4.0
0.0025	6.2	2.5
0.0010	10.5	2.8
0.000625	12.6	2.7
0.000500	16.9	3.9
0.000312	21.6	4.1

It has been shown, then, that all the alkali iodides are highly ionized in acetonitrile while zinc and cadmium iodides are only slightly ionized. Conductance data give the degree of dissociation of zinc iodide in a tenth molar solution as probably about 5×10^{-3} and that of cadmium iodide somewhat greater at that concentration, probably about 5×10^{-2}. If, therefore, the exchange reaction proceeds by an ionic reaction it would be expected that the relative rates of exchange would be in the order lithium: sodium: caesium: cadmium: zinc iodides as
$1 : 1 : 1 : 5 \times 10^{-2} : 5 \times 10^{-3}$.

It is important to note, however, that the conductivity measurements merely indicate the number of charged particles present in solution and do not give any indication of the identity of the particles. For the zinc and cadmium iodides the assumption was made that the particles were iodide ions and the singly-charged MI^+ ions. In view of the fact that both zinc and cadmium halides tend to form complexes in solution the validity of the assumption may be seriously questioned. Nevertheless, the relative rates indicated above for the exchange reactions should represent limiting values if the mechanism is an ionic exchange. That is, the concentration of iodide ions in the solution is equal to or less than that indicated by the dissociation constant, hence the exchange rate of an ion exchange reaction should be equal to or less than that indicated by the degree of ionization.

Conductance experiments indicated also that ions are present in an acetonitrile solution of iodine. Consequently, exchange through an ion mechanism could take place in the exchange of butyl iodide with elemental iodine. Again assuming Ostwald's dilution law and a molar conductance at infinite solution of 200 ohm^{-1} the dissociation constant was evaluated at a number of concentrations in Table V. If the iodine molecule dissociates into positive and negative ions, the assumption of 200 ohm^{-1} for the conductance at infinite dilution is quite sound, since the conductance of the iodide ion was reported to be 101 ohm^{-1}.

Table V. The dissociation constant for iodine.

Concentration moles/litre	Molar conductance ohm^{-1}	Dissociation constant
0.05	0.53	3.5×10^{-7}
0.01	1.42	5.1
0.002	5.60	1.6×10^{-6}
0.0004	23.7	6.4
0.00008	95.5	3.5×10^{-5}

Although the data in Table V do not fit the Ostwald dilution law exactly, the degree of ionization of iodine in a 0.05 molar solution is about 6 x 10^{-4}. If the exchange reaction with butyl iodide is strictly ionic, the exchange rate for iodine at that concentration should be about 7 x 10^{-4} of the rate for the exchange of butyl iodide with the alkali halides.

- The Exchange Experiments -

The Laboratory

Before experiments involving radioactive material could be done safely it was necessary to make considerable alterations to the existing laboratory facilities. All the walls were painted with a hard finish paint and all the wood-work was enamelled. Laboratory benches and tables were overlaid with masonite, linoleum, or glass. The inside of the fume hood was painted with Tygon plastic paint and the floor was laid with linoleum which was waxed from time to time.

In the "active" laboratory, active solutions were handled only with rubber gloves and were kept on large trays lined with blotting paper. The use of ordinary wash bottles and the practice of pipetting by mouth were strictly forbidden, those operations being performed instead with the aid of rubber bulbs or medical syringes. Items of equipment such as glassware, dessicators, stirring motors, thermostat baths, and hot plates which were subject to contamination, were not removed from the laboratory at any time.

The disposal of radioactive waste materials was not a serious problem because of the relatively short half-life of I^{131}. Active solutions were stored until radioactive decay had reduced the activity to a level safe enough for discharge down the laboratory drain. Suspensions of silver iodide, obtained when sample plates were cleaned, were treated in the same manner. Discarded reaction tubes which contained traces of activity were stored for several half-lives before being rejected from the laboratory. The same procedure was used in the disposal of other contaminated solids.

To insure its protection from accidental radioactive contamination the counting equipment was housed in a separate room adjacent to the "active" laboratory. The only radioactive materials allowed into this room were the sealed uranium "standard" sample and the active silver iodide samples.

In addition to the usual equipment, the laboratory was supplied with glassware and other equipment, including two centrifuges necessary for the manipulation of semi-micro quantities of materials. The following constant temperature baths were used:

0° C - ice-water freezing mixture
12-16° - acetic acid freezing bath

30-60° - water bath with standard controller
70-85° - oil baths with standard controller
100° - water vapour-bath
122° - tetrachloroethylene vapour-bath

The temperature of a vapour-bath was set by the boiling point of the liquid in the boiler and since the boiling temperature changed slightly with atmospheric pressure the bath temperatures were not quite constant. The variation was, however, less than 0.5°.

Materials:

Radioactive iodine, I^{131}, was obtained as carrier-free sodium iodide from the National Research Council Atomic Energy Project, Chalk River, at the rate of 0.50 mc. per month. A measured half life of 8.0 days indicated the absence of contamination by other radioactive materials.

Technical grade acetonitrile obtained from Brickman and Co., Montreal, was dried over anhydrous potassium carbonate and then distilled, the fraction boiling in the range 81.4 to 81.5°C being used as solvent in all the exchange reactions. Exhaustive tests proved that the solvent was stable and did not undergo reaction with sodium iodide even at high temperatures; these experiments are described in an Appendix. A determination was made of the thermal expansion of acetonitrile under normal sealed-tube conditions so that concentration corrections could be applied in calculations of rate constants at temperatures other than room temperatures. About twelve grams of acetonitrile was sealed in an eighteen millilitre dilatometer and the volume of the liquid measured at several temperatures. It was found that the volume of the solvent under those sealed-tube conditions was given by

$$V = V_o \left[1 + 0.0016 \; (t - t_o) \right]$$

for the range 0 to 100°C, where V_o is the volume of solvent measured at t_o°C.

Butyl iodide was obtained from Eastman Kodak and Brickman and Co. As received, it contained a small quantity of free iodine which was removed by shaking the butyl iodide with a little clean mercury. The colorless iodide was then distilled and the portion coming over in the range 128.4 to 128.6°C was used for the exchange reactions. It was necessary to store it in the dark to prevent subsequent liberation of free iodine.

Sodium iodide was Merck Reagent grade. Before use it was dried several days at 120°C.

Lithium iodide was obtained from Brickman and Co. as $LiI \cdot 3H_2O$. The water was driven from the hydrate at 130°C and the residue, containing some free iodine, was dissolved in acetonitrile, forming a solvate with the evolution of much heat. The solvate was recrystallized several times from acetonitrile and was used to prepare a stock solution of lithium iodide, the concentration of which was determined by gravimetric iodide analysis.

Caesium iodide and zinc iodide "Pure" were supplied by Brickman and Co. Both were dried overnight at 120°C before use.

Cadmium iodide "Crystals" was a Merck product.

Iodine was Merck Reagent grade.

Activation of an Iodide:

One of the iodides in an exchange reaction must be "activated", i.e. made radioactive, so that the exchange can be traced, and it was customary although not obligatory, to activate the inorganic iodide. The aqueous carrier-free solution obtained from Chalk River was diluted about twenty-fold with acetonitrile to give a solution the activity of which was determined approximately by evaporating a drop of it and counting the residue. The iodide solution to be used for one or more exchange experiments was activated by adding enough drops of the dilute, carrier-free solution to give a sufficiently high count. In this way zinc, caesium and lithium iodides were activated by exchange of the type

$$LiI + NaI^* \rightleftharpoons LiI + LiI^* + NaI$$

where the asterisk refers to the I^{131} atoms. A consideration of the relative initial concentrations makes it apparent that virtually all of the radioactivity is transferred from the sodium iodide to the lithium iodide. Suppose 200 ml. of 0.01 M LiI solution were innoculated with an activity of about 7×10^5 counts per minute. The total number of LiI molecules is

$$0.01 \times \frac{200}{1000} \times 6.06 \times 10^{23} = 1.2 \times 10^{21}.$$

The total number of NaI* molecules is given by the integration of

$$N = N_o e^{-\lambda t}$$

where N is the number of disintegrations per second at time <u>t</u>, there being N_o at $t = 0$. The value of λ is given by

$$= \frac{\ln 2}{t_{\frac{1}{2}}}$$

where $t_{\frac{1}{2}}$ is the half life of the isotope, ie. 8 days for I^{131}. Thus the total number of NaI* molecules added is

$$\left[-\frac{N_o}{\lambda} e^{-\lambda t} \right]_0^{\infty}$$

$$= \frac{N_o}{\lambda}$$

$$= 7 \times 10^5 \times \frac{8 \times 24 \times 60}{0.693}$$

$$= 1.2 \times 10^{10}$$

Hence the ratio of lithium iodide to sodium iodide concentration is

$$\frac{1.2 \times 10^{21}}{1.2 \times 10^{10}} = 10^{11}.$$

It is apparent first, that virtually all of the activity is transferred from the sodium iodide to the lithium iodide, and secondly, that the amount of sodium iodide contaminating the lithium iodide is negligible.

Iodine was activated in a similar manner.

Active butyl iodide was prepared by an analagous exchange with dry carrier-free radioactive sodium iodide. Several drops of the carrier-free solution were evaporated to dryness in a small distilling flask, butyl iodide was added and warmed occasionally for several hours and finally distilled off as active butyl iodide.

The Exchange Reaction:

In the exchange experiment an organic iodide is mixed with an inorganic iodide after one of them has been activated. After the reaction time has elapsed, the compounds are separated and the distribution of the radio-isotope is determined. The degree of exchange is calculated either from the decrease in activity of the active compound or from the gain in activity of the compound which was originally inactive.

The activity of an iodide may be expressed either as a specific activity or as a total activity. As the term implies the specific activity is proportional to the ratio of active to inactive iodine in the compound. It could be expressed in units of counts per minute per milligram of iodine, but it is more convenient to use the units of counts per minute per milligram of silver iodide since the iodine is counted as silver iodide. The units in the total activity method are simply counts per minute.

All of the exchange experiments in this investigation were based on specific activities rather than total activities, because of the following advantages:

The thick layer technique is similar to the specific activity method since the iodide is precipitated as silver iodide and a total recovery of the iodide is unnecessary. The difference is that the final deposit of silver iodide on the counting dish is so thick that the final count is independent of its weight and is a function only of its specific activity and area. When the method of preparing the sample is standardized the area of the deposit is fixed so the counts obtained from a number of samples are directly proportional to their specific activities. Thus, if care be taken that the weights be great enough it is unnecessary to weigh the silver iodide deposits. On the other hand, the specific activity method is based on a linear relation between count and weight, where again the area of the deposit is fixed. The latter method was preferred because it was thought that the count in the thick layer method might be unduly influenced by small variations in the physical state of the deposit.

The design of the vessel in which the exchange reaction took place depended on the velocity of the exchange reaction being studied. A rough division into "slow" and "fast" reactions was made, the slow reaction being one the rate of which was negligible at room temperature. For reactions of this type straight sealed tubes with capactities ranging from one to fifteen millilitres were used. Since the exchange reaction for slow reactions did not proceed appreciably at room temperature it was customary to mix the reactants of an exchange experiment at room temperature. The mixture was then divided into five approximately equal volumes which were sealed into glass reaction tubes in such a manner that the dead space in the tubes was small at the reaction temperature. The contents of the tubes were frozen (-41°) in an alcohol - dry ice bath before being sealed and were kept frozen until the tubes were placed in a constant temperature bath to start the exchange reaction.

Two types of reaction vessel were used for the "fast" reactions. Early in the investigation, glass-stoppered inverted Y-tubes were used, the reactants being thermostated in the separate arms until the vessel was inverted to mix the reactants at zero time. It was found that although these tubes were excellent for precise timing they were unsatisfactory because the reactants could not be thoroughly mixed. If the volume of the tubes had been increased to facilitate mixing, the dead space would have become prohibitively large. Consequently the Y-tubes were replaced by ordinary glass-stoppered erlenmeyer flasks. The reactants for an experiment were thermostated in separate flasks, combined at zero time and at appropriate intervals samples were withdrawn with a special rapid-delivery pipette and the reaction quenched by a separation of the two iodides.

Early in the investigation the separation of the organic and inorganic iodides was achieved by a benzene-water extraction of the reaction mixture, the butyl iodide going into the benzene layer and the inorganic iodide into the water layer. After the water layer was washed with benzene several times in the separatory funnel the inorganic iodide was precipitated by the addition of silver nitrate. It was possible to "analyse" or "count" the butyl iodide by precipitating the iodine with alcoholic silver nitrate. The precipitation took place very slowly at room temperature but went to completion in a few minutes at 80°C.

Later it was found possible to dispense with the time-consuming benzene-water separations when an analysis of only the inorganic iodide was to be made. When silver nitrate was added to a faintly acid solution of butyl iodide in an organic solvent (acetonitrile, methanol, or mixtures of these) a cloudiness developed only after about two minutes at room temperature and no silver halide could be centrifuged down even after five minutes. Hence it was apparent that the inorganic iodide could be precipitated directly from the reaction mixture since the precipitation, centrifuging, and decantation from the packed precipitate required less than one minute. To check the technique two experiments were done on the exchange of sodium iodide with butyl iodide, the direct precipitation being used in one and the benzene — water separation in the other. The rate constants were found to be 4.02 and 4.00. The excellent agreement demonstrated that the direct precipitation technique was acceptable for all subsequent inorganic iodide analyses.

The procedure for converting the crude silver iodide precipitate to a sample suitable for counting was as follows:

1. The silver iodide, originally precipitated in a 50 ml. centrifuge tube, was washed with 10 ml. of methanol to remove traces of butyl iodide which may have been adsorbed on the precipitate.

2. Residual methanol was removed by washing with 50 ml. of water.

3. The silver iodide was slurried up with concentrated nitric acid which was then heated to boiling to decompose any silver cyanide which may have been

precipitated from the acetonitrile solvent.

The hot suspension was diluted with water and the precipitate centrifuged down. The hot acid treatment apparently changed the crystal structure of the iodide so that it formed very fine suspensions in subsequent washings. In addition, the nitric acid oxidized traces of organic material in the precipitate which frequently caused discoloration of the silver iodide deposits on exposure to the light. Some silver iodide was decomposed by the acid but that was of little concern, since total recovery of the iodide was not needed when calculations were based on specific activities.

4. The silver iodide was then washed once with water and twice with methanol.

5. The precipitate was slurried up in about 5 ml. of methanol. The course particles settled out immediately and the remaining suspension was poured into the collar-plate cell shown in fig. 5 where it was evaporated to dryness under an infra-red or ordinary reflector spotlight bulb. Care was taken that the methanol did not boil during the evaporation. When evaporation was complete, the collar was lifted off leaving a smooth circular deposit of silver iodide on the weighed glass plate.

After the plate with its deposit was weighed, the sample was ready for counting.

The plate in the collar-plate unit is available at photographic supply houses as a cover glass for mounting 35 mm. color slides and is 50 mm. square and 1 mm. in thickness. Although made of soft glass it could be readily cleaned in a hot acid cleaning solution and used repeatedly. The collar was a section of 35 mm. glass tubing about 2 cm. long, having one end ground flat to make a suspension-tight joint when pressed firmly on the square plate.

Aluminum counting dishes were found to be unsatisfactory because frequently a reaction between the silver iodide deposit and the aluminum took place. In addition, uneven deposits were obtained because capillary action tended to concentrate the suspension around the edges of the dish.

It was very important that the methanol used in the latter part of the foregoing procedure be "Reagent" or equivalent grade. It was found that reasonably stable silver iodide suspensions could not be prepared using technical methanol or 95% ethanol presumably because the presence of a small amount of water caused the suspensions

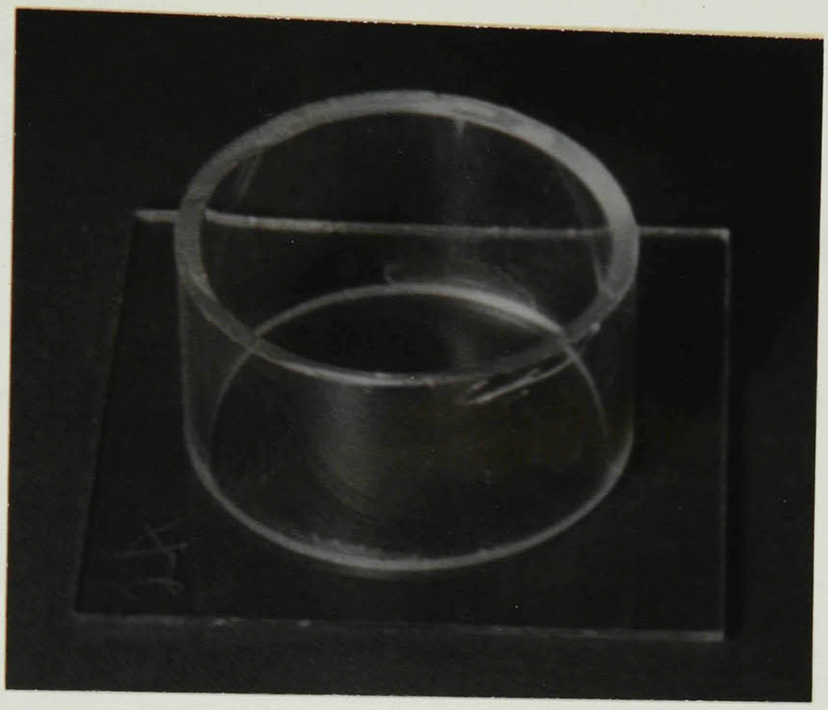

Fig. 5. Collar-plate cell for the evaporation of silver iodide suspensions.

Fig. 6. Silver iodide samples prepared from methanol and ethanol suspensions respectively.

to coagulate immediately. The nature of the suspension had a great influence on the final deposit of silver iodide. Fig. 6 shows photographs of typical silver iodide samples prepared from "reagent" methanol and 95% ethanol. It is clear that the methanol sample was quite smooth and regular whereas the other sample was so uneven that it failed to cover the bottom of the counting dish.

The Counting Apparatus

The counting assembly consisted of a geiger tube and preamplifier in a lead castle, a high tension source with a voltage regulator, a scaler, a register, and a timer.

The lead castle was of standard design having walls 1.5 inches thick with brackets on the inside to support the sample holder, geiger tube, and preamplifier. Two levels for the sample holder were possible, the sample being 1 or 2.5 cm. below the window of the geiger tube. The amplifier was mounted on a panel which fitted into the upper part of the castle where it was electrically shielded so that spurious impulses were not introduced into the scaler.

The geiger tubes were of the end-on type having mica or dural windows. Characteristics of three typical geiger tubes are summarized in Table VI. Tube #1 was least affected by voltages, but had a very short plateau, while tube #2 had a long plateau and consequently was used for the majority of the counting. The third tube evidently had been poorly constructed for it was very sensitive to voltage fluctuations and remained in operating condition for only a few hours.

Table VI. Geiger tube characteristics.

Tube	Type	Threshold volts	Operating volts	Plateau volts	Sensitivity % per 100 volts
1	mica	1175	1225	80	5
2	dural	1250	1300	200	10
3	mica	1400	1450	100	30

A transformer-rectifier power unit was built to replace the batteries originally supplied as a high tension source for the geiger tube. A Sola line-voltage regulator was inadequate to stabilize the input to the H.T. transformer and permitted the high tension output to vary over a range of 40 volts. To reduce this variation, a voltage regulator for high voltages was constructed. The circuit was essentially that recommended by Strong (27) and although slight drifts in voltage were observed over several hours operation, fluctuations were reduced to less than five volts.

The scaler was an Atomic Instruments Co. scale of 64, the output of which operated a mechanical register through a relay controlled by an interval timer. Checked against reliable watches and timers the timer was found to be accurate to a tenth of a second.

Although it was customary to "warm up" the counter on a uranium sample for at least an hour before doing any quantitative counting, it was found that the counter had to stabilize itself for each individual sample. Table VII shows the counting data for a sample which was counted steadily for 65 minutes; 35 one-minute counts were made followed by 15 two-minute counts. The count increased sharply in the first three minutes, even though the counter had been in continuous use for the preceding three hours. After five minutes of counting, the count was reasonably stable until the interval was changed to two minutes when the count immediately increased 0.7%. The mean deviation for the two-minute intervals was slightly less than for shorter intervals and in general the mean deviation was about 0.5%. As a result of the experiment, the counter was "warmed up" for five minutes, with each sample, before accurate counts were attempted.

Table VII. Count related to time of count.

Time minutes	Interval of count	Count/min. x 64^{-1}
0 to 1	one minute	208
1 2	"	213
2 3	"	214
3 4	"	214
4 5	"	214
5 to 15	one minute	215.3 ± 1.0
15 25	"	215.7 ± 1.4
25 35	"	215.6 ± 1.3
35 to 45	two minutes	217.0 ± 1.0
45 55	"	217.2 ± 0.6
55 65	"	216.9 ± 0.8

To show that it was possible to place a given sample under the geiger tube window and obtain a count that was truly representative of the sample the following experiment was done. A sample was counted, the holder withdrawn and the sample plate rotated through 90°, and the count repeated. The procedure was repeated three times, the sample being rotated through 360°, with counts made every 90°. The results shown in Table VIII have a mean deviation of less than 0.6%, which is approximately the same as the mean deviation for successive counts on a sample in a fixed position. Hence it was concluded that the count for a given sample was independent of its position.

Table VIII. Count related to position.

Position	Counts/min.
0°	17.5×10^{3}
90	17.5
180	17.7
270	17.7
360	17.5

An indication of the reproducibility of a series of counts is given by the data in Table IX, which were obtained by counting, and recounting an hour later, a series of five samples having the same specific activity. The deviations from the mean remained constant although the mean specific activity apparently increased. The apparent increase was probably caused by a drift in the H.T. voltage.

Table IX. Reproducibility of a series of counts.

Sample	Specific Activity Count/min./mgm. 1st count	Specific Activity Count/min./mgm. 2nd count
1	217	222
2	220	222
3	218	215
4	217	222
5	225	225
Mean	219.4±2.5	221.2±2.5

Since the sensitivity of the geiger tube was approximately 10% per hundred volts, the one percent change in count could have been caused by a drift of ten volts, a deviation scarcely noticeable on the H.T. voltmeter.

The counting period and specific activity of the sample were closely related. The length of time taken to count a particular sample was so chosen that the total error resulting from a combination of the errors in timing, voltage drifts and statistical fluctuations was at a minimum. To economize on working time, and to reduce errors from voltage drifts, it was desirable to count the sample in the shortest possible time. However, timing errors became appreciable on periods of less than one minute and it was necessary to have a total count of over 10,000 to reduce the error from statistical fluctuations to less than one percent. Hence it was desirable to have a sample with a high specific activity.

The effect of the background count was also reduced by increasing the activity of the sample. The background count without the castle was about 35 counts/min. and was reduced to one-half by the use of the castle. Although the background count increased slightly on prolonged use of the counter, it was negligible on samples having activities of over 5,000 counts/min.

Although it was desirable to have very active samples, an upper limit on the activity of a sample was set by errors arising from "coincident counting", wherein the geiger tube failed to resolve impulses which followed one another too closely. Because of coincident counting errors, counts from very active samples were too low, resulting in low specific activities. This is shown in Table X by the counting data for five samples which were prepared from a very active solution of sodium iodide. When the samples were very active the observed specific activities decreased with increasing weight and count, but after radioactive decay had reduced the activity of the samples the specific activities were found to be constant. The point at which the coincident errors became appreciable was not clearly defined. In general, however, coincident counting errors were avoided by choosing the weight and specific activity of the samples so that the count was less than 15,000 counts/min.

The weight of the sample had to be sufficiently large that weighing errors were negligible but not so large as to introduce errors from self-absorption in the sample. With an ordinary analytical balance weighing errors became appreciable on weights of less than 25 mgm. The self-absorption effect was of a more variable nature depending on both the weight of the sample and the nature of the deposit. As mentioned previously, the nature of the deposit was greatly affected by the presence of impurities in the alcohol used to make the silver iodide suspension from which the sample was prepared. Furthermore, if care was not taken to allow heavy particles of silver iodide to settle out before the decantation, they appeared in the final deposit and reduced the observed specific activity by several percent as a result of self-absorption. The data shown in the last column of Table X indicates that there was no self-absorption in smooth samples weighing up to 60 mgm.

Table X. The effect of coincident counting.

Weight of sample mgm.	Count/min.		Specific Activity count/min./mgm.	
	Jan.5	Jan.10	Jan.5	Jan. 10
20.3	10528	7013	519	345
25.5	13104	8805	513	345
29.6	15024	10213	508	345
53.9	25328	17637	497	346
61.4	30048	21125	488	344

In summary, the ideal sample was one which was perfectly smooth, weighed about 35 mgm., had an activity of about 10,000 counts/min. and a specific activity of about 300 counts/min./mgm. Such a sample required a counting period of only one or two minutes after the five minute warm-up. Consequently a series of six or seven such samples representing one kinetic exchange experiment could be counted in less than one hour.

Calculation of Results

The following derivation of the rate constant expression for the exchange reaction is an extension of that given by McKay (20), who assumed the exchange reaction could be written as

$$RI + I^{-*} \rightleftarrows RI^{*} + I^{-} .$$

Since not all the inorganic iodides are completely ionized in acetonitrile solution, and since the iodides are not all uni-univalent salts, let the exchange reaction be represented as

$$\underset{b}{RI} + \underset{c-x}{MI_{n-1}I^{*}} \rightleftarrows \underset{x}{RI^{*}} + \underset{a}{MI_{n}} \qquad (I)$$

where

MI_n is the inorganic iodide, *n* being 1, 2, 3,--.

RI is the organic iodide, and a and b are the molar concentrations of the inorganic and organic iodides respectively. Since RI* and $MI_{n-1}I^*$ refer to the molecules which are actually radioactive their concentrations in terms of molarity can be neglected. The total activity in the system is given by c, while x is the amount of activity transferred to the organic iodide; the units of both x and c may be expressed as counts per minute. It is quite accurate to write the radioactive inorganic as $MI_{n-1}I^*$, i.e. with only one atom of radioactive iodine per molecule, because for every active atom there are about 10^{11} inactive iodine atoms. Hence, the probability of finding two or more active iodines in one molecule is extremely small.

The total reaction rate for the exchange reaction is given by

$$V = k\, f(a,b) \qquad \text{(II)}$$

where k is a specific rate constant, and f(a,b) is some function dependent on the order of the reaction. It is important to notice that V, being independent of time, is a constant for a particular experiment, since it is dependent only on *k*, *a*, and *b*, which do not change during the course of the reaction.

The rate of the forward reaction as written is proportional to the total reaction and to the ratio of active to inactive inorganic iodide. It is inversely proportional to the number of iodine atoms per molecule of inorganic iodide. Similarly the rate of the reverse reaction is proportional to the total reaction and to the ratio of active to inactive organic iodide. Hence

$$\frac{dx}{dt} = \frac{c-x}{na}V - \frac{x}{b}V$$

Integration of the above expression with the boundary condition that $x = 0$ when $t = 0$ gives

$$V = \frac{nab}{(na+b)t} \ln \frac{1}{1-\frac{x}{c}\left(1+\frac{na}{b}\right)} \qquad \text{(III)}$$

In the above expression, x/c is the ratio of the total activity of the organic iodide to the total activity of the system. Experimentally it is difficult, as pointed out previously, to determine a total activity. The ratio is therefore expressed in terms of specific activities. The conversion is made by dividing the total activity terms by the concentration terms associated with each. Hence the ratio of specific activities is

$$A/A_0 = \frac{x}{b} \cdot \frac{na}{c}$$

A, the specific activity of the inorganic iodide, is determined experimentally as described previously, while A_0 is the specific activity of the inorganic iodide before exchange, i.e. it is the specific activity of a sample prepared from the unexchanged inorganic iodide. It is important to notice that the ratio of two specific activities is independent of the radioactive decay of the isotope, if the two samples are counted at approximately the same time.

In terms of specific activities (III) becomes

$$V = \frac{nab}{(na+b)t} \ln \frac{1}{1-A/A_0(1+b/na)} \qquad \text{(IV)}$$

If the calculations are based on the decrease in specific activity of the inorganic iodide, the degree of exchange, σ , at time t is given by

$$\sigma = \frac{1-(A/A_0)_t}{1-(A/A_0)_\infty}$$

$(A/A_0)_\infty$ may be determined experimentally by taking an equilibrium sample, or it may be calculated in the following manner. At equilibrium the activity originally present in na moles is evenly distributed throughout (b + na) moles. Hence

$$(A/A_0)_\infty = \frac{na}{b + na} \quad .$$

The degree of exchange at time t, therefore, is

$$\sigma = \left[1-(A/A_0)_t\right] \left(1 + \frac{b}{na}\right) \qquad \text{(V)}$$

Substituting (V) in (IV) gives

$$V = \frac{nab}{(na + b)t} \ln \frac{1}{1-\sigma} \qquad \text{(VI)}.$$

Since all the terms in (VI) except t and are constants for a given exchange experiment, there is a simple logarithmic relation between the degree of exchange, σ, and the time t. For this reason all exchange experiments have first order reaction - time curves. The order of the exchange reaction must be determined, as emphasized by McKay (loc.cit.) by changing a and b so that the precise form of the function V may be determined, and the order ascertained. If the reaction is first order

$$V = ka \quad \text{or} \quad V = kb \ ;$$

if second order

$$V = kab \ ;$$

if third order

$$V = ka^2b \quad \text{or} \quad V = kab^2 \ .$$

Hence, for a second order reaction the specific rate constant is

$$k = \frac{n}{(na+b)t} \ln \frac{1}{1-\sigma} \qquad \text{(VII)}$$

If the inorganic halide is uni-univalent (VII) reduces to the form

$$k = \frac{1}{(a+b)t} \ln \frac{1}{1-\sigma} \qquad \text{(VIII)}$$

If, instead of basing the calculations on the decrease in activity of the inorganic iodide, they are based on the gain in activity of the organic iodide, the degree of exchange is given by

$$\sigma = A'_t/A'_\infty$$

where A' and A'_∞ are the specific activities of the organic iodide at time t, and at infinite time respectively. The exchange is also given by

$$\sigma = \frac{(A'/A_0)_t}{(A'/A_0)_\infty}$$

and since $(A'/A_0)_\infty = \frac{a}{b+na}$

therefore $$\sigma = (A'/A_0)_t(1+b/na). \qquad \text{(IX)}$$

When the rate constants for an exchange reaction have been evaluated at several temperatures, the parameters in the modified Arrhenius equation (28)

$$\log \frac{k}{\sqrt{T}} = A - \frac{E}{4.57T}$$

may be evaluated, where E is the activation energy of the reaction.

It is apparent from a consideration of the general rate expression (VI) that the activation energy of an exchange reaction may be determined even if the order of the reaction is not known, since the reaction - time curves for all exchanges reaction are first order. Any order, say first order, may be assumed for the reaction and the "rate constant" evaluated at various temperatures. If a and b are the same in all the experiments the Arrhenius plot is a straight line, from the slope of which the activation energy may be calculated.

It was, therefore, desirable to maintain the values of a and b constant, so that any error in the determination of the reaction order would not introduce an error into the determination of the activation energy of the reaction.

It was necessary to plan the exchange experiments in such a manner that the errors in the determinations would be a minimum. Hence it was necessary to decide which iodide would be activated and which iodide would be counted. In addition, the ratio of organic iodide concentration to inorganic iodide concentration had to be chosen in such a manner that the errors would be at a minimum.

The exchange experiments could be planned in any of the following ways:

1. The organic iodide is activated and the inorganic iodide counted. The degree of exchange is given by

$$\sigma = (A/A_o')_t \, (1+na/b)$$

where $\underline{A}$ and $\underline{A}_o'$ are the specific activities of the inorganic iodide, and the organic iodide at zero exchange. As before, a/b is the ratio of the concentrations of inorganic to organic iodide. If a/b is much greater than one the exchange is characterized by a small change in A/A_o and consequently the error inherent in $\underline{A}$ is magnified in the value calculated for σ. The error in $\underline{\sigma}$ may be reduced by making a/b very small, but this is somewhat undesirable because the exchange reaction is then one between a small amount of inactive inorganic iodide and an excess of active organic iodide, which would entail the use of a large amount of activity in a volatile compound. The health hazard associated with such an experiment would thus be unduly large. However, the exchange of cadmium iodide with butyl iodide was studied in this manner.

2. The organic iodide is activated and the exchange based on the decrease in the activity of the organic iodide. Counting the organic iodide is undesirable because it necessitates the analysis of the organic iodide, a tedious procedure involving benzene-water separations.

3. The inorganic iodide is activated and the organic iodide counted. This method is undesirable for the same reason as the previous one.

4. The inorganic iodide is activated and the count based on the decrease in activity of the inorganic iodide. In contrast with methods 2 and 3 the direct precipitation method can be used to separate the inorganic iodide from the reaction mixture. The degree of exchange is given by

$$\sigma = (A/A_0)_t \, (1+na/b) \, .$$

Again the magnitude of the error in $\underline{\sigma}$ caused by an error in $\underline{A}$ is dependent on the ratio a/b. If a/b is large the error is magnified. This is shown in Table XI in which the error in $\underline{\sigma}$ caused by a 1% error in $\underline{A}$, is evaluated for various a/b ratios at various degrees of exchange. It is apparent that the error in $\underline{\sigma}$ is reduced when a/b is decreased and furthermore, it is apparent that the errors are smaller at high percentage exchanges.

Table XI. The error in $\underline{\sigma}$ caused by a 1% error in the determination of $\underline{A}$, evaluated for various b/a ratios and for various degrees of exchange.

b/a	Percent error at an exchange of 10%	35%	60%	80%
10	109	32.6	17.3	12.7
4	49	13.3	7.3	5.2
1	19	5.5	2.3	1.5
0.25	11	2.8	1.1	0.6
0.10	10	2.1	0.9	0.4

When the concentration of the active inorganic iodide is much smaller than that of the organic iodide the amount of activity used in an exchange experiment is small. As a result, the health hazard is small and the level of the activity of the waste materials from an exchange experiment is low, facilitating their disposal. Consequently, most exchange experiments were planned in the following manner: the inorganic iodide was activated, the organic iodide was in excess, and the calculation of the degree of exchange was based on the decrease in activity of the inorganic iodide.

Care was taken to allow the exchange reaction to proceed to at least 20% exchange because, as evident from Table XI, the errors at low percentage exchanges were very high. In general it was desirable to have the samples in the range 35 to 70% for greatest accuracy. As apparent from Table XI, an a/b ratio of 0.25 had an error of approximately one half that of the one-to-one ratio and little precision was gained by making the ratio 0.10. Hence in most of the experiments the a/b ratio was about 0.2. Under those conditions the precision in σ was slightly less than that associated with A.

- The Exchange Results -

Before extensive exchange experiments were done it was necessary to show that the exchange results calculated from a decrease in activity of the inorganic iodide were consistent with those calculated from the gain in activity of the organic iodide. To show this, both the inorganic and organic iodides were analysed in an exchange of lithium iodide with butyl iodide. Table XII shows that the sum of the specific activities for each reaction sample agreed with the count for the zero sample within one percent. The rate constants calculated from the inorganic analysis were in good agreement with those calculated from the organic iodide analysis.

It has been well established that the exchanges between aliphatic halides and alkali halides are second order reactions (20, 14, 15, 16, 12, 23). This was confirmed for the reaction between lithium iodide and butyl iodide in acetonitrile when the concentrations of the two reactants were varied at least two-fold in two exchange experiments at one temperature.

Table XII.[†]

The exchange of 0.025 M butyl iodide with
0.025 M lithium iodide at 29.2°C.

Time min.		A A'	A_0	A/A_0 A'/A_0	$\sigma\%$ $\sigma'\%$	k k'
35	Inorg.	104.0		0.813	37.4	16.1
	Org.	23.3		0.183	36.6	16.5
	Total	127.3	127.0	0.996		
40	Inorg.	102.2		0.805	39.0	14.9
	Org.	26.1		0.205	41.0	15.9
	Total	128.3	127.0	1.010		
50	Inorg.	98.3		0.775	45.0	14.4
	Org.	29.1		0.229	45.8	14.7
	Total	127.4	127.0	1.004		
70	Inorg.	90.0		0.708	58.4	15.1
	Org.	35.9		0.283	56.6	14.3
	Total	125.9	127.0	0.991		
90	Inorg.	82.3		0.648	70.4	16.2
	Org.	43.8		0.345	69.0	15.7
	Total	126.1	127.0	0.993		

Inorganic mean: 15.6±0.6

Organic mean: 15.4±0.7

[†] In this table and all subsequent tables, unless specifically stated otherwise, the units for specific activities A, A_0, and A', are counts per min. per mgm. of silver iodide, the rate constants are second order rate constants with units of litres, mole^{-1}, hour^{-1}, the degree of exchange is designated by σ, and values based on organic iodide counts are designated with a prime, thus A', k', and σ'.

The rate constants calculated from the second order rate expression for a univalent inorganic halide exchange

$$k = \frac{1}{(a+b)t} \ln \frac{1}{1-\sigma}$$

were found to be reasonably constant. The data are presented in Table XII, and Table XIII, exp. 88.

Since lithium iodide exchanges readily with butyl iodide the experiments were made at relatively low concentrations and low temperatures. Table XIII shows the results of exchange experiments made at four temperatures from 0° to 47.5°C.

Experiments 87, 89, 90, and 92 in Table XIII show that calculations based on the equilibrium distribution of the activity represented by the zero sample are quite sound. In those four experiments the reaction was allowed to proceed to equilibrium, and the equilibrium samples showed 100% exchange within experimental error. Equilibrium samples were used thereafter as checks on the reliability of the concentration figures, and in some experiments the exchange calculations were based on the equilibrium sample rather than on zero exchange.

Table XIII.

The exchange of lithium iodide with butyl iodide.

Experimental conditions	Time hr.	A	A_0	σ %	k	
0.01 M LiI*	5.5	124.4	150	20.5	0.708	
0.05 M BuI	9.5	104.5	"	36.3	0.790	
0°C	9.5	108.2	"	33.3	0.711	
	19.0	82.8	"	53.9	0.680	
Exp. 87	Inf.	24.5	142	99.4		0.700±0.013
0.01 M LiI*	1.5	106.5	140	28.8	3.73	
0.05 M BuI	2.0	95.7	"	38.0	3.97	
14.2°C	2.5	89.2	"	43.4	3.79	
	4.0	72.9	"	57.7	3.57	
Exp. 89	4.5	65.2	116	64.2	3.79	
	Inf.	21.5	"	97.8		3.77±0.10
	min.					
0.01 M LiI*	35	106.6	176	47.2	18.2	
0.05 M BuI	40	102.6	"	50.0	17.3	
29.2°C	60	81.2	"	64.6	17.3	
	80	66.5	"	74.7	17.2	
Exp. 88	100	57.7	"	80.8	16.5	17.3±0.4
0.01 M LiI*	40	43.3	124.5	91.1	103	
0.025 M BuI	35	45.8	"	88.3	105	
47.5°C	40	43.2	"	91.2	104	104±1
Exp. 90,	Inf.	33.1	116.0	100.2		
92.						

Table XIV.

The exchange of sodium iodide with butyl iodide.

Experimental conditions	Time hr.	A	A_o	σ%	k	
0.01 M NaI*	1.0	301	360	16.9	0.710	
0.25 M BuI	1.5	281	"	22.9	0.667	
0°C	2.5	237	"	35.6	0.643	
	3.5	189	"	49.4	0.750	
Exp. 67	5.0	138	"	64.2	0.788	0.712±0.046
0.01 M NaI*	11	423	507	23.1	0.682	
0.025 M BuI	16.5	403	"	28.7	0.584	
0°C	26	293	426	43.7	0.630	
Exp. 65	40	239	"	61.3	0.680	0.644±0.037
0.01 M NaI*	1.5	176	230	30.5	4.04	
0.05 M BuI	2.0	162	"	37.6	3.93	
14.2°C	2.5	147	"	45.2	4.01	
Exp. 72	3.0	135	"	51.4	4.00	3.99±0.04
0.01 M NaI*	1	344	498	43.3	16.2	
0.25 M BuI	2	255	"	68.2	16.4	
29.2°C	3	211	"	80.7	15.6	
Exp. 66	4	189	"	87.0	14.6	
	5	169		92.6	14.9	15.5±0.7
		A'				
0.050 M NaI*	0.5	70	249	42.4	14.7	
0.025 M BuI	1.0	110	"	66.3	14.5	
29.2°C	1.5	137	"	82.3	15.4	
	2.0	147	"	89.0	14.7	
Exp. 70	2.5	154	"	92.8	14.0	14.7±0.3
	min.	A				
0.01 M NaI*	15	193	249	40.8	93.2	
0.0125 M BuI	20	181	"	49.6	91.3	
47.5°C	30	160	"	64.5	92.2	
Exp. 69	Inf.	141	"	78.7	103	92.2±0.6

Table XIV shows the results for the exchange between sodium iodide and butyl iodide. Since the reaction velocities for the sodium iodide exchanges were nearly the same as those for the lithium iodide exchanges, the experiments were done at the same temperatures.

Within the limits of experimental error, the exchange of sodium iodide with butyl iodide was a second order reaction. At 0°C the concentration of butyl iodide was increased ten-fold, bringing about an increase in rate constant of ten percent which cannot be considered significant, since there was a five percent deviation from the mean associated with each value. At 29.2°C, the concentration of butyl iodide was doubled and the increase in rate constant was not significant.

The exchange of caesium iodide with butyl iodide was studied in the same temperature range as the exchanges of sodium and lithium iodides. The results are presented in Table XV. Experiments 94 and 101 in Table XIII show that the second order rate expression was adequate for this exchange. It was

Table XV.

The exchange of caesium iodide with butyl iodide.

Experimental conditions	Time min.	A	A_0	σ%	k	
0.0076 M CsI*	240	305	359	17.3	0.825	
0.050 M BuI	330	288	"	22.7	0.810	
	480	265	"	30.1	0.777	
0°C	600	249	"	35.1	0.751	
Exp. 100	780	228	"	41.8	0.723	0.777±0.040
0.0093 M CsI*	105	132	171	27.1	3.04	
0.050 M BuI	120	127	"	30.5	3.07	
12.2°C	240	96.6	"	51.5	3.06	
Exp. 99	300	86.5	"	58.5	2.97	3.04±0.03
0.0076 M CsI*	20	264	360	30.8	19.2	
0.050 M BuI	30	233	"	40.6	18.1	
	40	203	"	50.3	18.3	
29.1°C	50	177	"	58.6	18.4	
Exp. 101	60	152	"	66.7	19.1	18.6±0.5
0.005 M CsI*	30	24.1	A_∞ 52.8	45.6	22.2	
0.050 M BuI	60	36.0	"	68.2	20.8	
29.0°C	90	42.2	"	79.8	19.5	20.8±0.9
Exp. 94	Inf.	52.8	"			
0.00465 M CsI*	20	40.0	191.0	20.9	71.3	
0.0050 M BuI	30	56.7	"	29.5	72.3	
39.9°C	40	67.2	"	35.1	67.1	
Exp. 98	50	80.3	"	42.0	67.8	69.6±2.2
	Inf.	191.0				

found more convenient to base the exchange calculations for experiments 94 and 98 on infinity samples instead of on zero samples because of the low solubility of caesium iodide in acetonitrile.

The rate constants for the exchanges of the three alkali halides with butyl iodide are summarized in Table XVI, where corrections for the thermal expansion of the solvent are applied. Table XVII shows the values of the parameters of the Arrhenius lines of the three alkali halides. The method of least squares was used to evaluate the constants and the probable error associated with each.

Preliminary results showed that the rate of exchange of butyl iodide with zinc iodide was quite different from its rate of exchange with the alkali iodides. To obtain a measureable rate of exchange at ordinary temperatures it was found necessary to increase the concentrations of the inorganic and organic iodides at least five-fold.

The order of the exchange reaction of zinc iodide with butyl iodide was determined at 100°C, the data for three experiments at that temperature

Table XVI.

Corrected rate constants for the exchanges of lithium, sodium and caesium iodides with butyl iodide.

	t°C	k	correction	$k_{corrected}$
LiI	0	0.700	0.960	0.672
	14.2	3.77	0.984	3.71
	29.2	17.3	1.007	17.4
	47.5	104	1.036	107.8
NaI	0	0.712	0.960	0.683
	14.2	3.99	0.984	3.93
	29.2	15.5	1.007	15.6
	47.5	92.2	1.036	95.5
CsI	0	0.777	0.960	0.746
	12.2	3.04	0.980	2.98
	29.0	19.7	1.008	19.9
	39.9	69.6	1.024	71.2

Table XVII.

Arrhenius line parameters.

Iodide	A	$-B \times 10^{-3}$
Lithium	13.22±0.04	18.2 ± 0.1
Sodium	12.83±0.11	18.0 ± 0.1
Caesium	13.65±0.06	18.7 ± 0.1

being shown in Table XVIII. Within the experimental error the exchange of butyl iodide with zinc iodide was found to be second order. Since zinc is bivalent the value of n in the general second order rate expression is two, hence the rate expression for the exchange of zinc iodide is

$$k = \frac{2}{(2a + b)\,t} \ln \frac{1}{1 - \sigma} .$$

Table XIX shows the exchange results for zinc iodide for the temperature range 47.5 to 122°C.

Cadmium iodide, like zinc iodide, exchanged slowly with butyl iodide. The organic iodide was the active iodide in these experiments, which made possible accurate measurements at low percentage exchanges, as shown by experiments 58 and 59 in Table XXI.

However, experiments to determine the order of the reaction showed that the second order rate expression was not applicable. This is shown in Table XX, where it is apparent that the concentration of the inorganic iodide had an unduly large influence on the reaction rate. It was found that when

$$V = ka^2b$$

Table XVIII.

The effect of concentration on the rate constant for the exchange of zinc iodide with butyl iodide at 100°C

Experimental conditions	Time hr.	A	A_o	σ%	k	
0.01 M ZnI_2^*	2.5	171	220	26.6	0.915	
	3.5	149	218	38.0	1.005	
0.25 M BuI	4.5	138	"	44.0	0.955	
	6.0	123	"	52.4	0.918	
Exp. 84	7.0	114	"	62.9	1.025	0.964±0.041
0.01 M ZnI_2^*	1.5	271	385	30.9	0.950	
0.50 M BuI	2.0	247	"	37.3	0.900	
	4.0	158	"	61.5	0.918	
Exp. 80	5.0	123	"	70.9	0.952	
	6.0	96	"	78.2	0.977	0.939±0.024
0.025 M ZnI_2^*	1.0	237	265	12.6	0.898	
0.25 M BuI	1.5	226	"	17.7	0.866	
	2.5	196	"	31.2	0.995	
Exp. 73	3.5	176	"	40.7	0.994	
	7.0	121	253	63.8	0.968	0.944±0.050

Table XIX

The exchange of 0.05 M zinc iodide with 0.50 M butyl iodide

Experimental conditions	Time hr.	A	A_0	σ%	k	
47.5°C	46	130	140	8.4	6.36 x 10^{-3}	
	101	122	"	15.4	5.52	
Exp. 48	200	108	"	27.2	5.28	
	214.5	103	"	31.5	5.88	(5.76±0.33)10^{-3}
60.0°C	34	130	157	20.6	2.26 x 10^{-2}	
	55	120	"	28.3	2.02	
Exp. 76	79	105	"	39.8	2.14	
	98	99	"	44.2	1.99	(2.10±0.10)10^{-2}
81.0°C	4.5	201	233	16.4	0.133	
	6	188	"	23.2	0.147	
	8	183	"	25.7	0.124	
Exp. 75	11	167	"	34.0	0.126	
	13	154	"	40.7	0.134	
	17	142	"	46.8	0.110	0.129±0.009
	min.					
122.0°C	60	93.6	220	69.0	3.90	
	80	77.4	"	78.0	3.78	
	100	59.8	"	87.3	3.98	3.89±0.07
Exp. 83	Inf.	34.3	"	101		

Table XX.

Evaluation of the second and third order rate constants for the exchange of butyl iodide with cadium iodide at 82°C.

Experimental conditions	Time hr.	σ%	k_2†	k_3‡
0.05 M CdI_2	3	24.9	0.547	10.9
0.25 M BuI*	5	37.5	0.537	10.6
	7	49.8	0.563	11.3
Exp. 60	9	57.8	0.548	11.0
			mean: 0.549	10.9
0.025 M CdI_2	10	36.8	0.306	12.3
0.25 M BuI*	24	67.3	0.312	12.5
	26	69.0	0.302	12.0
Exp. 56	52	90.3	0.300	12.0
			mean: 0.305	12.2
0.025 M CdI_2	12	26.1	0.288	11.5
0.125 M BuI*	30.5	55.2	0.302	12.0
	41	66.5	0.305	12.2
Exp. 61	48.5	72.8	0.307	12.2
			mean: 0.301	12.0

† $$k_2 = \frac{2}{(a+b)t} \ln \frac{1}{1-\sigma} \quad (1, \text{mole}^{-1}, \text{hr.}^{-1})$$

‡ $$k_3 = \frac{2}{a(a+b)t} \ln \frac{1}{1-\sigma} \quad (1^2, \text{mole}^{-2}, \text{hr.}^{-1}).$$

was substituted in the general rate expression (VI) giving

$$k = \frac{2}{a\ (2a + b)t} \ln \frac{1}{1 - \sigma}$$

the values for the rate constant were reasonably constant. Hence, the exchange between cadmium and butyl iodides was shown to be a third order reaction, in which the exchange rate was proportional to the square of the concentration of cadmium iodide.

The exchange of cadmium iodide with butyl iodide was studied over the temperature range 30 to 82°C. The results are shown in Table XXI. To obtain an accurate evaluation of the activation energy the concentration of cadmium iodide was held constant at the four temperatures.

Radioactive iodine exchanged slowly with butyl iodide in acetonitrile solution. Experiments 108 and 109 in Table XXII showed that the reaction is second order.

The exchange calculations in Table XXII are based on the decrease in activity of the iodine. The

Table XXI.

The exchange of cadmium iodide with butyl iodide.

Experimental conditions	Time hr.	A	A_0	σ% †	k_3 ‡	
0.05 M CdI_2	94	14.3	171	10.1	7.56 x 10^{-2}	
0.50 M BuI*	142	21.3	"	15.0	7.63	
30.0°C	181	27.0	"	19.0	7.76	
Exp. 59	258	36.5	"	25.6	7.62	(7.64±0.06)10^{-2}
0.05 M CdI_2	11	8.0	108	8.9	5.66 x 10^{-1}	
0.50 M BuI*	18.5	13.2	"	14.7	5.72	
48.0°C	37	22.9	"	25.5	5.32	
Exp. 58	61	33.6	"	37.3	5.13	(5.46±0.23) 10^{-1}
0.05 M CdI_2	11	12.1	112	15.1	1.70	
0.25 M BuI*	37	34.1	"	42.7	1.72	
60.0°C	48	40.0	"	49.9	1.65	
Exp. 62	71	51.8	"	64.8	1.69	1.69±0.02
0.05 M CdI_2	3	24.6	138	24.9	10.9	
0.25 M BuI*	5	37.0	"	37.5	10.6	
82°C	7	49.2	"	49.8	11.3	
Exp. 60	9	57.1	"	57.8	11.0	10.9±0.2

† $\sigma = (A/A_0)_t(1 + 2a/b)$

where A is the specific activity of the CdI_2

and A_0 is the specific activity of the unexchanged butyl iodide.

‡ $k_3 = \frac{2}{a(2a+b)t} \ln \frac{1}{1-\sigma}$

Table XXII

The exchange of iodine with butyl iodide

Experimental conditions	Time hr.	A	A_o	σ%	k	
0.10 M BuI	40	118	166	43.5	0.191	
0.025 M I_2^*	48	111	"	49.8	0.191	
69.7°C	56	106	"	54.3	0.187	
Exp. 107	63	99	"	60.5	0.197	
	65	99	"	60.5	0.191	0.191±0.002
0.100 M BuI	12	152	194	30.9	0.412	
0.025 M I_2^*	15	161	217	38.7	0.408	
81.0°	20	133	194	47.2	0.424	
Exp. 105	24	127	194	51.8	0.406	0.412±0.005
0.100 M BuI	5.5	131	194	48.6	1.61	
0.025 M I_2^*	7.0	124	201	57.2	1.62	
100°C	9.0	110	201	67.8	1.68	
Exp. 106	12.0	97	201	77.8	1.67	1.65±0.03
0.100 M BuI	1.00	133	176	36.6	6.06	
0.025 M I_2^*	1.00	133	"	36.6	6.06	
122°C	1.25	127	"	41.7	5.75	
Exp. 108	1.25	125	"	43.2	6.02	
	1.33	124	"	44.3	6.25	6.05±0.11
0.04 M BuI	1.0	290	319	27.3	5.33	
0.04 M I_2^*	1.0	282	"	34.8	7.12	
122°C	1.5	271	"	45.0	6.65	
Exp. 109	1.5	275	"	41.3	5.93	
	2.0	273	"	43.5	4.75	
	2.0	261	"	54.3	6.52	6.05±0.71

iodine in samples of reaction mixture was reduced with sulfurous acid, in the water-benzene separations, and samples of radioactive silver iodide were prepared from the aqueous layer in the usual manner.

Experiments were done at four temperatures from 69.7° to 122°C. Sodium thiosulfate titrations of the reaction mixtures, at the highest temperature, showed that iodine did not substitute into the organic iodide under the conditions necessary for exchange.

A summary of the exchange results for the reactions of butyl iodide with zinc and cadmium iodide and iodine is given in Table XXIII where corrections for thermal expansion of solvent are applied to the observed rate constants. Since the rate for the exchange of cadmium iodide is proportional to the square of the concentration of cadmium iodide the usual correction factor was squared. Table XXIV shows the values of the parameters of the Arrhenius lines for the three exchange reactions. The method of least squares was used to evaluate the constants and the error associated with each.

A summary of the data for the exchange of butyl iodide with lithium, sodium, caesium, zinc, and cadmium

Table XXIII

Corrected rate constants for the exchanges of zinc and cadmium iodides and iodine with butyl iodide.

Compound	t°C	k	corrn.	$k_{corr.}$
Zinc Iodide	47.5	5.76×10^{-3}	1.036	5.97×10^{-3}
	60.0	2.10×10^{-2}	1.056	2.22×10^{-2}
	81.0	1.29×10^{-1}	1.090	1.41×10^{-1}
	122.0	3.89	1.155	4.49
Cadmium Iodide	30.0	7.64×10^{-2}	1.016	7.76×10^{-2}
	48.0	0.546	1.072	5.84×10^{-1}
	60.0	1.69	1.112	1.88
	82.0	10.9	1.188	13.0
Iodine	69.7	0.191	1.072	0.205
	81.0	0.412	1.090	0.449
	100.0	1.65	1.120	1.85
	122.0	6.05	1.155	6.99

Table XXIV. The Arrhenius line parameters for the exchange of butyl iodide with zinc and cadmium iodides and iodine.

	A	$-B \times 10^{-3}$
ZnI_2	11.45±0.09	21.9±0.1
CdI_2	12.38±0.04	20.6±0.1
I_2	9.60±0.30	17.5±0.1

Table XXV. A summary of the data for the exchange of butyl iodide with lithium, sodium, caesium, zinc, and cadmium iodides, and iodine.

	Activation energy Kcal. / mole	Calculated rate constant 25°C
Lithium iodide	18.2	11.4
Sodium iodide	18.0	10.2
Caesium iodide	18.7	13.1
Zinc iodide	21.9	4×10^{-4}
Cadmium iodide	20.6	4×10^{-2}*
Iodine	17.5	4×10^{-3}

* Since the exchange of cadmium iodide is a third order reaction, the value of its rate constant is not directly comparable with the other values in the table.

iodides and iodine is given in Table XXV. Values for the rate constants for the exchanges at 25°C were calculated from the Arrhenius lines. Since the exchange of cadmium iodide is a third order reaction its rate constant is not directly comparable with the rate constants for the exchange of butyl iodide with the other compounds.

- DISCUSSION -

Molecular weight determinations and conductance measurements have shown that the alkali iodides are highly ionized in acetonitrile, while zinc and cadmium iodides, and iodine, are only slightly ionized. The exchange of the alkali iodides with butyl iodide takes place very readily, but the exchange of butyl iodide with the other three is very slow. It would appear, then, that the rate of exchange is related to the degree of ionization.

If the rate of exchange is governed by the degree of ionization, the rate constants for the exchange of butyl iodide with the three alkali iodides should have been identical since all three behave as strong electrolytes and are highly ionized in acetonitrile solution. Exchange experiments of the three iodides showed this to be true, the rate constants at 25°C being 11.4, 10.2, and 13.1 for lithium, sodium, and caesium iodides respectively.

The agreement among the three alkali iodides was reasonably good when the rate constants were calculated on a concentration basis; an activity correction makes it even better. The concentration of the inorganic iodide in the exchange experiments with lithium and sodium iodides was 0.1 molar for both compounds, but the concentration of caesium iodide used varied from 0.0093 to 0.00465 M. Hence, to make the exchange rates for the three compounds strictly comparable it is necessary to apply an activity correction to the caesium iodide value. The magnitude of the correction is somewhat uncertain because the concentration of the caesium iodide in the exchange experiments varied from experiment to experiment. However, it seems reasonable, from the data in Table XV, to assume a concentration of 0.005 M on which to base the activity correction at 25°C. Both molecular weight determinations and conductivity measurements indicated that the activity coefficients of the iodides decreased about 15% with an increase in concentration from 0.005 M to 0.01 M. A decrease in the rate constant for exchange was also observed when the concentration of the alkali iodide was increased in exchange experiments designed to determine the order of the reactions between the alkali iodides and butyl iodide. In general, the extent of the observed decrease in rate agrees with the magnitude of the change in activity coefficient for a given change in concentration. Hence, the rate constant found for caesium iodide at 25°C should be decreased about 15% to make it comparable with the other two iodides; the three rate constants are then 11.4, 10.2 and 11.1 for lithium, sodium and caesium iodides respectively.

The mean deviation of the three rate constants for the exchange of butyl iodide with the alkali iodides is about 4% from the mean value of 10.9. Since the mean deviation for the experimental determination of a rate constant was about 5%, it may be concluded that the rate constants for the three highly ionized inorganic iodides are identical within experimental error. This is strong support for an ion mechanism of exchange, between organic and inorganic iodides, but it does not rule out the possibility of exchange by some other mechanism when the inorganic iodide is not highly ionized, for example, with zinc and cadmium iodides.

An expression relating rate of exchange of a slightly ionized inorganic iodide to the degree of exchange may be derived on the basis of the following successive exchange reactions:

$$\text{(a)}\quad MI_{n-1}I^* + I^- \rightleftharpoons MI_n + I^{*-} \qquad \text{(IX)}$$

$$\text{(b)}\quad I^{*-} + BuI \rightleftharpoons I^- + BuI^*$$

It is reasonable to assume that the exchange reaction of the inorganic iodide with iodide ion takes place very readily and as a result the exchange of the iodide ion with butyl iodide may be regarded as the rate controlling step.

Let the total concentration of inactive inorganic iodide be a, the concentration of iodide ion from the ionization of the inorganic iodide be i, and the concentration of the inactive organic iodide be b. The concentration of non-ionized inorganic iodide is (a-i), but since i is so very much smaller than a for a slightly ionized inorganic iodide, the concentration of the non-ionized iodide may be assumed to be a. The concentration of the active molecules is negligible in terms of molarities, hence only differences or ratios of concentrations of active molecules need be considered. The concentration of active compounds is expressed as counts per minute. Let the concentration of active inorganic iodide be c initially; after y counts per minute have exchanged to the ions in solution, and x counts per minute to the organic iodide, the count of the inorganic iodide is c-y-x, but since the concentration of ions is so small, the y term in c-y-x may be neglected.

Hence the rate of exchange of the first exchange reaction

$$\underset{c-x}{MI_{n-1}I^*} + \underset{i}{I^-} \rightleftharpoons \underset{a}{MI_n} + \underset{y}{I^{*-}} \qquad \text{(IXa)}$$

is given by

$$\frac{dy}{dt} = k_1 \left[i(c-x) \right] - k_1' \left[ay \right] \qquad \text{(X)}$$

where k_1 and k_1' refer to the forward and reverse reactions respectively. The rate of the forward reaction is slower than that of the reverse reaction by a factor of 1/n; the probability of a collision between $MI_{n-1}I^*$ and I^- resulting in radioactive exchange is reduced by 1/n because, as pointed out previously, the probability of finding more than one active iodide atom in an inorganic iodide molecule is extremely small. Hence

$$\frac{dy}{dt} = k_1 \left[i(c-x) - nay \right] \qquad \text{(XI)}$$

Similarly, it can be shown for the second exchange between butyl iodide and iodide ion,

$$\underset{y}{I^{*-}} + \underset{b}{BuI} \rightleftharpoons \underset{i}{I^{-}} + \underset{x}{BuI^{*}} \qquad \text{(IXb)}$$

that

$$\frac{dx}{dt} = k_2\left[yb - xi\right]$$

Since the rate of increase of activity for the organic iodide must be equal to the rate of decrease of activity for the inorganic iodide, then

$$\frac{dy}{dt} = \frac{dx}{dt}$$

When $\underline{y}$ is eliminated from (X) and (XI) and k_1 assumed to be very much greater than k_2

$$\frac{dx}{dt} = ik_2\left[\frac{b}{na} (c-x)-x\right] \qquad \text{(XII)}$$

When (XII) is integrated with the boundary condition that $x = 0$ when $t = 0$, it is found that

$$k_2 = \frac{an}{i(na+b)t} \quad \ln \frac{1}{1-\sigma} \qquad \text{(XIII)}$$

where $\underline{\sigma}$ is the degree of exchange of the inorganic iodide with butyl iodide. It is important to notice that k_2 is the rate constant for the exchange of butyl iodide with iodide ions, and as such is independent of the nature of the inorganic iodide in the exchange reaction.

The rate constant calculated from the degree of exchange of butyl iodide with various inorganic iodides is

$$k = \frac{n}{(na+b)t} \ln \frac{1}{1-\sigma}$$

Hence

$$\frac{k}{k_2} = \frac{i}{a} = \alpha$$

where $\underline{\alpha}$ is the degree of ionization of the inorganic iodide. It would appear, then, that the rate constant calculated from experimental data should be less than the rate constant for the iodide ion - butyl iodide exchange by a factor equal to the degree of ionization of the inorganic iodide if the exchange takes place only through an intermediate exchange with iodide ions. Since k_2 is the rate constant for the exchange of butyl iodide with iodide ions, the value of k_2 for the exchange in acetonitrile is given by $\underline{k}$ for the exchange of the highly ionized alkali iodides with butyl iodide. Thus k/k_2 can be evaluated for the exchange of butyl iodide with zinc and cadmium iodides, and a comparison with the degree of ionization of each of the iodides will, therefore, show whether the exchange occurs by only an ionic mechanism. Although molecular iodine is not an inorganic iodide it may be treated in the same manner as zinc and cadmium iodides.

Conductance measurements indicated that the degree of ionization of zinc iodide in a 0.1 M solution in acetonitrile is about 4×10^{-3}. The rate constant $\underline{k}$, for the exchange reaction at that concentration was found to be less than that of the alkali iodides by a factor of about 4×10^{-5}, i.e. $k/k_2 = 4 \times 10^{-5}$. Since the observed rate of exchange was less than that expected on the basis of the conductance measurements, no mechanism other than the ionic exchange need be postulated for the exchange of zinc iodide with butyl iodide.

The fact that the exchange of zinc iodide was slower than predicted from conductance measurements may be attributed to an over-simplified interpretation of the conductance measurements. It was assumed that all the ions in a zinc iodide solution were either ZnI^+ ions or iodide ions. This is probably not true because zinc (and cadmium) halides tend to form complex ions in solution. It is probable then, that the concentration of iodide ions in solution was less than that indicated by conductance measurements.

The third order rate constant found for the exchange of cadmium iodide with butyl iodide is of considerable interest. The nature of the rate equation for the exchange indicates that the abnormality of the reaction is associated with the cadmium iodide reactant. When the rate equation for the exchange

$$k = \frac{2}{a(2a+b)t} \ln \frac{1}{1-\sigma} \qquad \text{(XIV)}$$

is compared with the rate equation for the exchange of butyl iodide with iodide ion

$$k_2 = \frac{2a}{i(2a+b)t} \ln \frac{1}{1-\sigma}$$

it is apparent that

$$i = \frac{k}{k_2} a^2 \qquad \text{(XV)}$$

That is, the concentration of the iodide ion is proportional to the square of the concentration of the inorganic iodide.

Conductance data, by their failure to fit the Ostwald dilution law, also support the suggestion that the concentration of iodide ions is not directly proportional to the concentration of the inorganic iodide. The suggestion that the iodide ion concentration is dependent on the square of the concentration of the inorganic iodide implies that the iodide ions are formed by some second order process, possibly the collision of two cadmium iodide molecules.

Conductance measurements on acetonitrile solutions of cadmium iodide indicate that most of the ions are complex ions (29) which may have been formed by the interaction of two or more cadmium iodide molecules. Hittorf (32) observed that the transport number for the cadmium iodide cation was less than zero, while the transport number for the anion was greater than one, and concluded that the ionization process was

$$2\ CdI_2 \rightleftharpoons Cd^{++} + CdI_4^{=} .$$

McBain (33) presented evidence to show that cadmium iodide exists in solution as $(CdI_3^-)_2$ and Cd^{++}. It is not unlikely, then, that a very low concentration of iodide ions could be formed by a bimolecular process.

From equation (XV)

$$k/k_2 = i/a^2 = \alpha/a \; .$$

k/k_2 for the exchange of cadmium iodide with butyl iodide is 4×10^{-3} and the value for α/a at the same concentration, 0.05 M, is about 2. As with the zinc iodide exchange, the exchange rate expected from the conductance measurements is greater than the observed rate of exchange and no mechanism other than the ionic exchange need be postulated for the exchange of cadmium iodide with butyl iodide.

As with the exchange of zinc iodide, the deviation of the observed rate of exchange from the rate predicted from the conductance measurements, may be attributed to an over-simplified interpretation of the conductance data.

As mentioned previously, although iodine is not an inorganic iodide of the type MI_n, the relation between the exchange rate and degree of ionization developed for the slightly ionized inorganic iodides is applicable to the iodine exchange. The conductance measurements indicated that the degree of ionization, at the concentration of iodine used in the exchange experiments, was about 7×10^{-4} . Hence, on the basis of the conductance measurements the ratio k/k_2 should have been the same, and indeed it was found to be 4×10^{-4} . There is little doubt, then, that the exchange of iodine with butyl iodide occurs through an intermediate exchange with iodide ions.

The better agreement with iodine than with zinc and cadmium iodides is probably to be attributed to the simplicity of the process involved in the dissociation of the iodine molecule, in contrast to a complex behaviour in the ionization of zinc and cadmium iodides.

Considered as a whole, the data for the rates of exchange of the five inorganic iodides and iodine with butyl iodide leave little doubt that the ionic exchange mechanism is the one and only mechanism for the exchange of butyl iodide with these compounds.

Since the exchange reactions have been shown to occur by an ionic mechanism, the rate determining step being the exchange of iodide ion with butyl iodide, it is not immediately apparent why the activation energies found for the six exchange reactions should not be identical.

The activation energies found for the exchanges of the alkali iodides with butyl iodide were very similar, being 18.2, 18.0, and 18.7 kcal. per mole for lithium, sodium, and caesium iodides respectively. As with the absolute exchange rates, the value for caesium iodide was higher than that for the other two. It may be attributed to the same cause, namely a change in activity coefficient with concentration. Care was taken to maintain the concentrations of lithium iodide and sodium iodide constant in the experiments leading to an evaluation of the activation energy, but unfortunately this precaution was not taken with exchanges involving caesium iodide. At lower temperatures the concentration of caesium iodide was 0.0093 M, and at the highest temperature the concentration was only 0.00465 M. Consequently the activity coefficient of the caesium iodide was high at the high temperatures and as a result the rate of exchange was slightly increased. When corrections are applied to make the caesium iodide activities at all the temperatures comparable with the activities of the lithium and sodium iodides, the activation energy for the caesium iodide exchange is reduced to 18.2 kcal. per mole.

Hence, the relative activation energies for the exchange of the butyl iodide with the three alkali iodides (0.01 M) may be taken to be 18.2, 18.0, and 18.2 kcal. per mole for lithium, sodium, and caesium iodide respectively. The probable error in these determinations by the method of least squares was about 0.5% which agrees favourably with the mean deviation from the mean of the three values. It may be concluded, therefore, that the activation energies were identical within experimental error.

The activation energy found for the zinc iodide - butyl iodide exchange was 21.9 kcal. per mole, i.e., 3.8 kcal. higher than the value for the butyl iodide-iodide ion exchange represented in exchange reactions with the alkali iodides. To explain the difference, it is necessary to recall how the activation energy for a reaction is determined experimentally. Considering the exchange of zinc iodide with butyl iodide, four experiments were done at four different temperatures, a rate constant calculated for each temperature, and the activation energy calculated from the slope of the Arrhenius line obtained from a plot of log $k/T^{\frac{1}{2}}$ against $1/T$. From the definition of activation energy, the reaction proceeds faster at a higher temperature because there is a higher concentration of "activated" molecules, or molecules having sufficient energy to react. However, with slightly ionized zinc iodide, a secondary effect may be caused by a rise in temperature. The degree of ionization probably increases and it is apparent from

$$\frac{k}{k_2} = \alpha$$

that the rate constant k is probably increased. Since the increase in ionization is essentially an increase in activity of the zinc iodide, the increase is given by

$$\frac{d\ln f}{dT} = \frac{-\bar{L}}{RT^2}$$

where f is the activity, and $\bar{L}$ the relative partial molar heat content of the solute. Since $\bar{L}$ isthe difference in heat content of the solute between the value for a given solution and that in a standard state, which is usually taken to be infinite dilution for a slightly ionized salt, the relative partial molar heat content is nearly the same as the heat of ionization of the salt.

Integration of the above expression gives the relation between activity and temperature:

$$\ln f = \frac{\bar{L}}{RT} + \text{Constant}$$

Since this is a logarithmic relation, the changes of activity of the zinc iodide caused by temperature changes do not cause the Arrhenius line to be other than a straight line, but merely change the slope of the line indicating a higher activation energy.

Hence the activation energy found for the zinc iodide - butyl iodide exchange may be expected to be greater than the true activation energy for the butyl iodide exchange with an iodide ion by a factor approximately equal to the heat of ionization of the zinc iodide molecule.

Similarly, the activation energy found for the exchange of cadmium iodide with butyl iodide is greater than the value for the butyl iodide - iodide ion exchange. The increase of 2.4 kcal. per mole was less than the increase for zinc iodide probably because complex ion formation in the cadmium iodide solutions is more pronounced.

It is interesting to note that the activation energy for the exchange of butyl iodide with iodine was slightly less than that found for the iodide ion exchange with butyl iodide. Apparently the heat of ionization of iodine in acetonitrile is slightly less than zero. It must be emphasized that the heat of ionization is a general term including both the energy necessary to break the iodine bond, and the heat released during the solvation of the resulting ions. Although it has been shown (30) that the negative iodide ion is solvated only slightly in acetonitrile, it is quite possible that the positive ion may be highly solvated. Indeed, the positive ion may form a stable co-ordination compound with acetonitrile in which the pair of unbonded electrons held by the nitrogen in the acetonitrile forms a co-ordinate covalet bond with the positive iodide ion. The energy released in the formation of such a bond could be sufficient to reduce the over-all heat of ionization to zero, or even make it negative.

Another important consideration in the exchange of iodine with butyl iodide is the possibility that exchange occurs with the positive rather than the negative iodide ion. The activation energy for such an exchange would probably be less than for the negative iodide ion exchange. However, a consideration of the relative ease of approach of the two ions to the centre of reaction in the organic molecule, makes the positive ion exchange seem less probable. According to Pauling (34) carbon and iodine have equal values on the scale of negativity, but the carbon-iodine bond in aliphatic iodides has a finite dipole moment in which the carbon atom is positive and the iodine negative. Thus, a negative ion approaches the carbon atom in the Walden inversion mechanism more easily than does a positive ion. Hence the positive iodide ion exchange seems improbable.

APPENDIX

THE EXCHANGE OF SODIUM IODIDE WITH AROMATIC IODIDES

Before the major problem of this thesis was begun, a study of the exchange of various aromatic iodides was initiated in an attempt to obtain fundamental data on carbon - iodine bond energies and reactivities. However, after some work had been done it was found that the exchanges took place with so much difficulty that it was virtually impossible to obtain precise kinetic data for the reactions. Nevertheless, the results of the work are considered important enough to be recorded here since they show that exchange of alkali iodides with aromatic iodides is possible, and that relative rates of exchange of compounds having different substituents on the benzene ring agree with generally accepted views of the properties of benzene derivatives.

The exchange of aromatic halides with alkali halides has not been widely studied because of the difficulty with which exchange occurs. Using I^{128}, McKay (6) reported that phenyl iodide, p-nitroiodobenzene, and p-iodoaniline did not exchange with sodium iodide at 100°C in fifteen minutes in ethyl alcohol, nor did sodium bromide exchange with phenyl bromide (35). Only the negative ionizing iodine in diphenyl iodonium iodide exchanged with iodide (36).

Aluminum bromide was found to exchange with both bromobenzene and α-bromonaphthalene (37). However, the exchange which took place in the temperature range 16° to 200°C, was always accompanied by secondary reactions, and increasing amounts of benzene and nitrobenzene as solvent suppressed both exchange and secondary reactions. No exchange was observed between the same organic bromides and potassium, cupric, and antimony (ous) bromides.

The reactivity of aromatic halides is apparently increased by the presence of negative groups in the benzene ring. Thus, the exchange of 2,4-dinitrobromobenzene with lithium bromide took place so readily that it was possible to make a kinetic study of the exchange reaction (16). Similarly, rapid exchange of both potassium iodide and iodine takes place with 2,6-diiodophenol, 4,6-diiodophenol, 3,5-diiodo-p-cresol, 2,4,6-triiodophenol at 50°C in 50% methanol (38). It was also shown that diiodotyrosine exchanged readily in aqueous solution with potassium iodide and more readily with elemental iodine.

Short-lived radioisotopes were used in most of the foregoing investigations, the isotopes being I^{128} with a half-life of about 24 minutes, and the bromine tracer was a mixture of several isotopes with half-lives of about thirty hours. For this reason, it was impossible to follow the reactions more than a few hours, but now with the availability of the eight day I^{131} it is possible to study reactions which require weeks for measurable exchange to occur.

It was proposed, then, to make a complete study of the exchanges of sodium iodide with the iodobenzene, o-, m-, and p-iodotoluenes and o-, m-, and p-iodobenzoic acids. Hence, not only would the relative effects of the subsituent group in the three positions ortho, meta, and para to the iodine in the benzene ring be determined, but it was hoped to compare the effects of the meta-directing carboxyl group with the effects of the ortho-directing methyl group.

EXPERIMENTAL and RESULTS

The experimental procedures for the exchange of aromatic iodides with sodium iodide were essentially the same as for the exchange of butyl iodide with various inorganic iodides.

The main difference was that the experimental conditions for the exchange of the aromatic iodides were very much more severe than those for the butyl iodide exchanges. Most of the reactions were studied at temperatures ranging from 185° to 230°C, and the duration of each experiment was of the order of weeks rather than hours. The following thermostat baths were used, in addition to those previously mentioned:

157°C	hexanol vapour-bath
185°C	aniline vapour-bath
207°C	tetralin vapour-bath
216°C	benzyl acetate vapour-bath
200-230°C	electric furnace

Before accurate results could be obtained, a suitable solvent had to be chosen for the exchange reaction. Ethylene glycol diacetate, which was used by Sugden and his co-workers (16) was found to be unsuitable, because preliminary exchange experiments showed that sodium iodide reacts with it under the conditions necessary for the exchange of iodobenzene. For example, when 0.05 M sodium iodide in ethylene glycol diacetate was heated at 210°C for three hours a light colored crystalline precipitate appeared, and on further heating the precipitate darkened in color and increased in quantity. Since it was desirable to have a solvent with a relatively low vapour pressure at 200°C, the suitability of a series of high boiling solvents was examined. Hexanol, cyclo-hexanol, and ethylene glycol were rejected because they reacted with sodium iodide. Benzyl alcohol and cyclopentanone were unsuitable because there was some reaction with sodium iodide, and nitrobenzene was rejected because sodium iodide was only slightly soluble in it. A series of mixtures of hexanol and benzene proved unsuitable because the mixtures, homogeneous at room temperature, formed two layers at high temperatures. There was also some reaction with sodium iodide.

Both ethanol and acetonitrile were suitable from a solubility standpoint, sodium iodide being quite soluble in both, and p-iodobenzoic acid, apparently the least soluble organic iodide, formed a 0.05 molar solution at room temperature. Ethanol was rejected in favour of acetonitrile because the vapour pressure of ethanol at 200°C is approximately thirty atmospheres, while that of acetonitrile is only about thirteen atmospheres. Furthermore, the aromatic exchange reaction probably occurs more readily in acetonitrile than in ethanol, as indicated in Table XXIV by the data for the exchange of butyl iodide with sodium iodide in the two solvents.

Table XXIV. The effect of solvent on the exchange rate of butyl iodide with sodium iodide at 29°C.

Solvent	Time hr.	Exchange
CH_3CN	1	47%
EtOH	1	8
CH_3CN	4.5	91
EtOH	4.5	32

Additional tests were made to prove the suitability of acetonitrile as solvent. To ascertain whether there was any reaction of sodium iodide or organic iodides with acetonitrile, the experiments outlined in Table XXV were done. Iodide determinations were made by silver nitrate titrations after carbon dioxide had been bubbled through the solutions to remove any HCN present. The results indicate that, within experimental error, no inorganic iodide was lost under these conditions.

Table XXV. Iodide recovery from CH_3CN solutions.

NaI	RI	Experimental conditions	$AgNO_3$ titer
0.10 M	------	control	10.60ml.
0.10	------	20 hr. at 210°	10.64
0.10	0.2 M $p\text{-}NO_2C_6H_4I$	"	10.67
0.10	0.1 M $p\text{-}IC_6H_4COOH$	"	10.57

A second experiment was done to test for exchange between iodide and cyanide. Samples were withdrawn from time to time from a 0.2 M solution of active sodium iodide in acetonitrile, thermostated at 207°C. A benzene-water separation of the sample was done and the water layer evaporated to dryness, following which the white residue of inorganic salts was dissolved in water, and silver iodide and silver cyanide, if any, precipitated by the addition of silver nitrate. The specific activity of the precipitate was then determined. The results presented in Table XXVI indicate that there was no iodide - cyanide exchange at 207° for a period of over 400 hours. Hence, acetonitrile was used for all exchange reactions because the least soluble reactants could be dissolved to give working concentrations, the vapour pressure was low enough for reasonable safety, and there were no detectable reactions between it and the iodides.

Table XXVI. A test for CH_3CN - NaI reaction

Reaction time hr.	Specific activity count/min./mgm.
0	80 (calc.)
40	80.0
85	76.8
133	78.8
181	78.5
424	79.7
If completely exchanged	0.8 (calc.)

Reagents:

Sodium iodide was Merck Reagent grade. Before use it was dried several days at 120°C.

p-Iodobenzoic acid was prepared from p-aminobenzoic acid by diazotization. Because the crude product could not be recrystallized from ordinary solvents, it was purified by sublimation. m.p. 273°; reported 270°C.

p-Nitroiodobenzene was prepared by diazotizing p-nitroaniline. Recrystallized several times from ethanol, it melted at 172°C; reported 173°C.

Iodobenzene and o-iodotoluene were Eastman Kodak products.

Activation of an iodide:

The active iodide in all the aromatic exchange reactions was sodium iodide. It was activated in the manner previously described.

The exchange reaction:

All aromatic exchange reactions were classed as "slow" reactions and therefore the reaction vessels used were straight sealed tubes. At very high temperatures, the reaction tubes were made from combustion tubing for additional safety; otherwise ordinary thin-walled tubing was used.

Benzene-water separations were used throughout. When the sodium iodide was to be counted, the water layer from the separation was acidified, the iodide precipitated with silver nitrate, and the sample of silver iodide prepared for counting in the usual manner.

When it was desired to count the organic iodide it was necessary to reduce the aromatic iodide with a strong reducing agent. At first, sodium metal was used, the metal being sealed in a reaction tube with the benzene solution of the aromatic iodide and heated overnight at 200°C. After the reduction was complete, ethanol was added to the contents of the tube to remove the residual sodium metal, the resulting suspension was centrifuged, and the iodide precipitated from the supernatant liquid by the addition of silver nitrate. The silver iodide was then prepared for counting in the usual way.

Later, the sodium metal reduction was replaced by Raney nickel-aluminum reduction (40) in which the benzene layer containing the aromatic iodide was made alkaline with alcoholic potassium hydroxide, a small amount of nickel-aluminum alloy added, and after the initial reaction had subsided the mixture was heated for several hours. If a quantitative recovery of the iodide was required the reduction was done under reflux, but for most purposes quantitative recovery was not essential and the reductions were done in covered beakers. When the reduction was complete, the catalyst was centrifuged down, the superantant liquid acidified with nitric acid, and silver nitrate added to precipitate the silver iodide from which the sample was prepared for counting as before.

Calculation of results:

The calculations were based on either the decrease in activity of the active sodium iodide, or on the gain in activity of the aromatic iodide. The degree of exchange was given as before by

$$\sigma = (1 - A/A_0)_t \, (1 + a/b)$$

for the decrease in activity of sodium iodide and

$$\sigma = (A/A)_{\sigma t}(1 + a/b)$$

for the increase in activity of the organic iodide.

Exchange Results:

Preliminary exchange experiments between sodium iodide and iodobenzene, p-nitroiodobenzene, and p-iodobenzoic acid were done. The data shown in Tables XXVII, XXVIII, and XXIX demonstrated that exchange with these three compounds was possible under rather severe temperature conditions.

Table XXVII. p-Iodobenzoic acid exchange with NaI.

NaI moles/litre	RI moles/litre	Temp. °C	Time hr.	σ%
0.10	0.04	210	15	12
0.05	0.10	210	168	26
0.05	0.10	210	288	37
0.05	0.10	207	336	61
0.05	0.10	185	504	6

Table XXVIII. p-Nitroiodobenzene exchange with NaI

NaI moles/litre	RI moles/litre	Temp. °C	Time hr.	σ %
0.05	0.25	210	16	48

Table XXIX. Iodobenzene exchange with NaI.

NaI moles/litre	RI moles/litre	Temp. °C	Time hr.	σ %
0.05	0.50	210	96	0.5
0.05	0.50	210	168	3.3
0.05	0.50	210	312	7.7
0.05	0.50	185	72	0.0

After it had been shown that exchange of sodium iodide with aromatic iodides was possible, a complete study of the exchange of sodium iodide with the three iodotoluenes was begun, starting with o-iodotoluene. Fig. 7 shows the reaction-time curves at four temperatures for the exchange of sodium iodide with o-iodotoluene, the concentrations being 0.2 and 0.5 molar respectively. At the highest

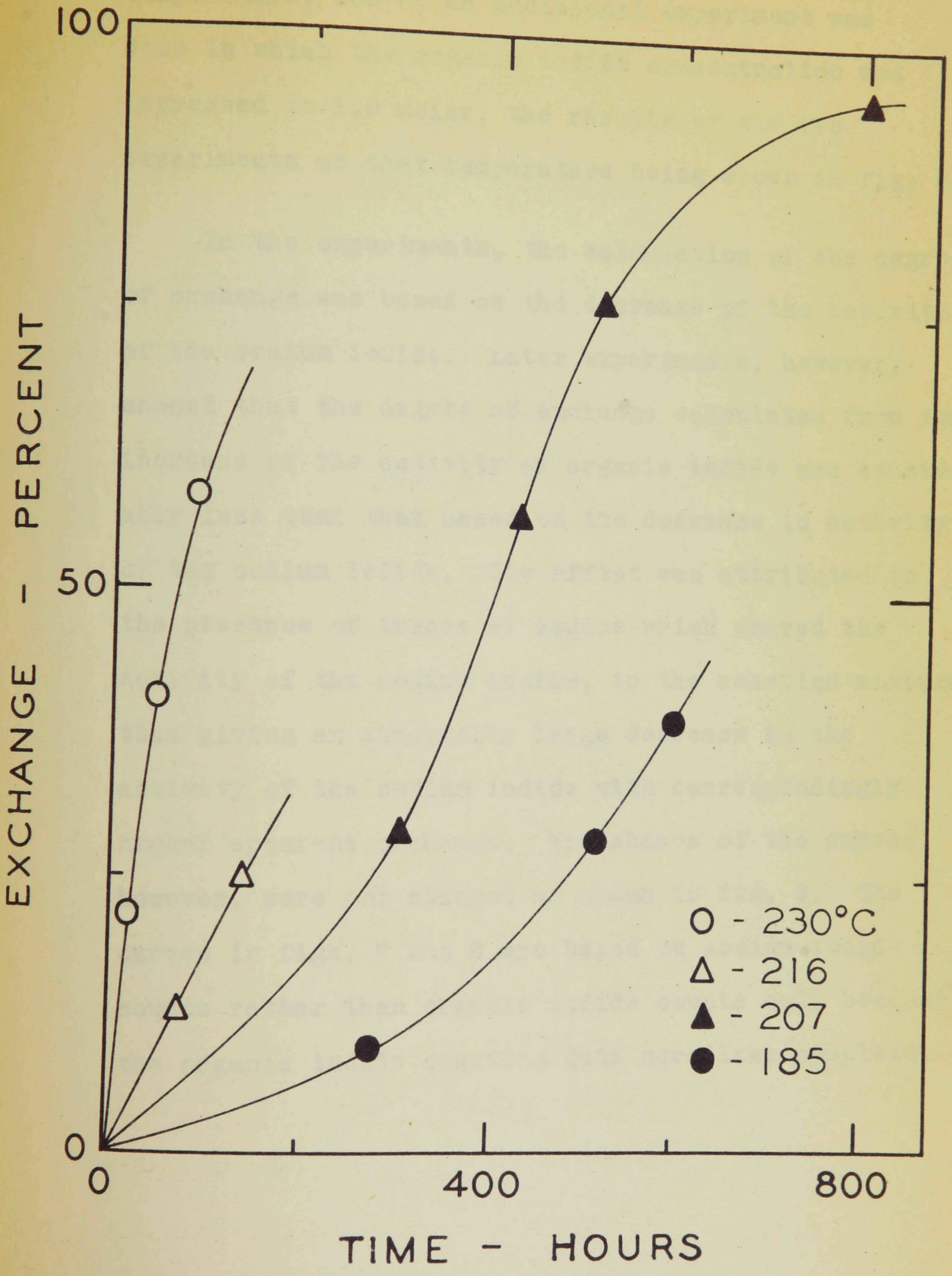

Fig. 7. The exchange of 0.2 M sodium iodide with 0.5 M o-iodotoluene.

temperature, 230°C, an additional experiment was done in which the organic iodide concentration was increased to 1.0 molar, the results of the two experiments at that temperature being shown in fig. 8.

In the experiments, the calculation of the degree of exchange was based on the decrease of the activity of the sodium iodide. Later experiments, however, showed that the degree of exchange calculated from the increase of the activity of organic iodide was considerably less than that based on the decrease in activity of the sodium iodide. The effect was attributed to the presence of traces of iodine which shared the activity of the sodium iodide, in the reaction mixtures, thus giving an abnormally large decrease in the activity of the sodium iodide with correspondingly higher apparent exchange. The shapes of the curves, however, were not changed as shown in fig. 9. The curves in figs. 7 and 8 are based on sodium iodide counts rather than organic iodide counts only because the organic iodide counting data were less complete.

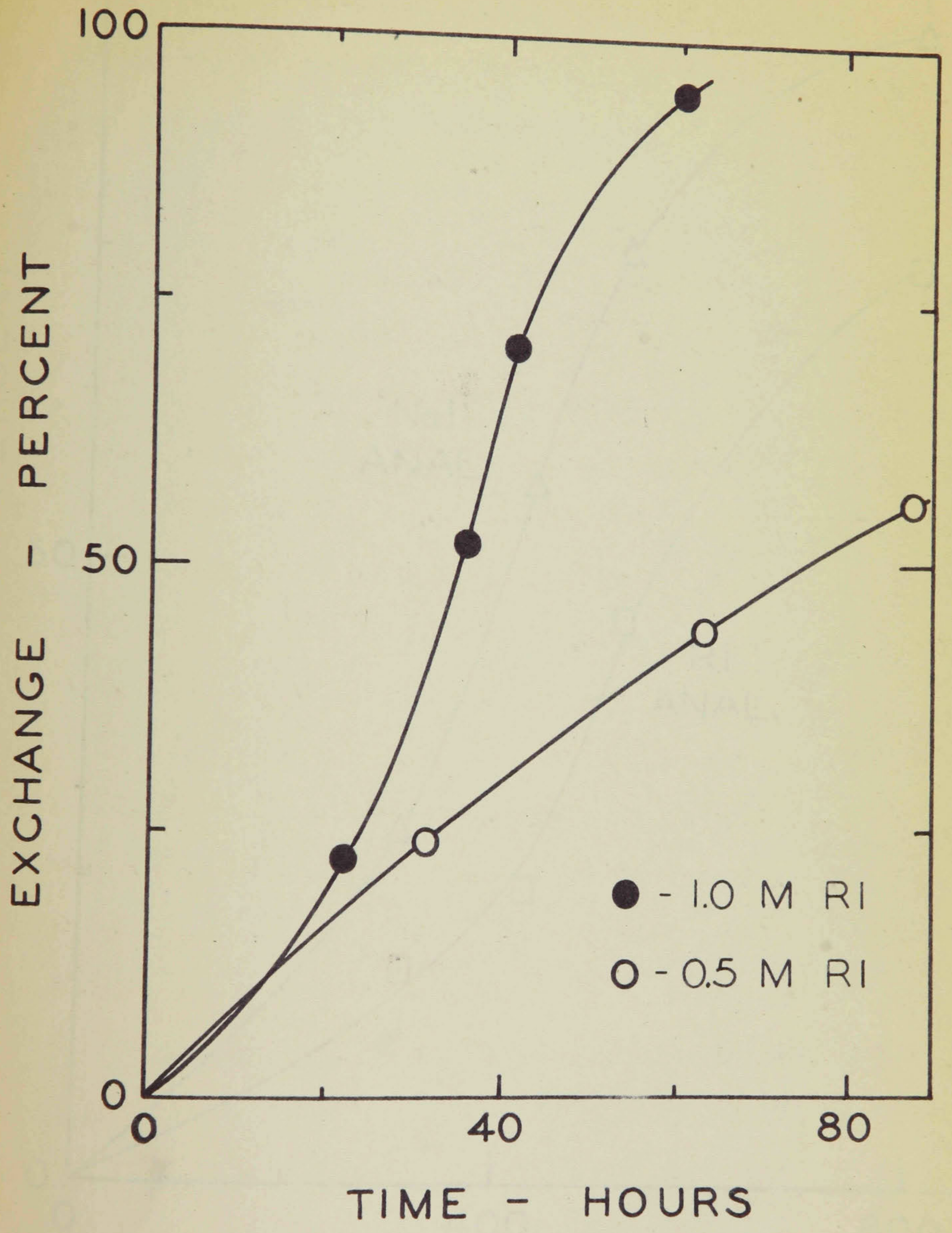

Fig. 8. The exchange of 0.2 M sodium iodide with 1.0 M and 0.5 M o-iodotoluene at 230°C.

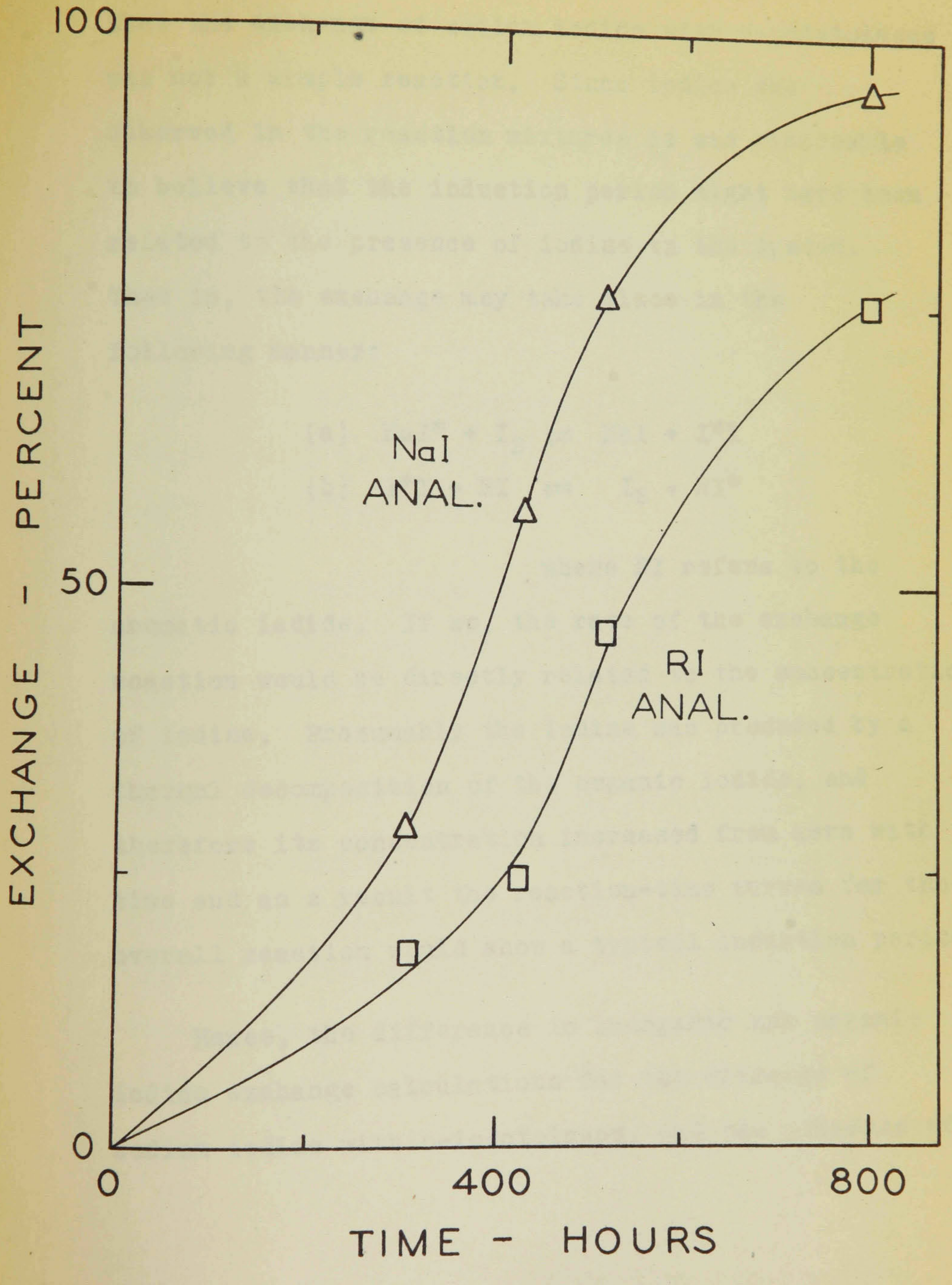

Fig. 9. Inorganic and organic iodide analyses for the exchange of 0.5 M o-iodotoluene with 0.2 M sodium iodide at 207°C.

The induction periods in figs. 7 and 8 indicate that the exchange of sodium iodide with o-iodotoluene was not a simple reaction. Since iodine was observed in the reaction mixtures it was reasonable to believe that the induction period might have been related to the presence of iodine in the system. That is, the exchange may take place in the following manner:

$$\text{(a)} \quad NaI^* + I_2 \rightleftharpoons NaI + I^*I$$

$$\text{(b)} \quad I^*I + RI \rightleftharpoons I_2 + RI^*$$

where RI refers to the aromatic iodide. If so, the rate of the exchange reaction would be directly related to the concentration of iodine. Presumably the iodine was produced by a thermal decomposition of the organic iodide, and therefore its concentration increased from zero with time and as a result the reaction-time curves for the overall reaction would show a typical induction period.

Hence, the difference in inorganic and organic iodide exchange calculations for the exchange of sodium iodide with o-iodotoluene, and the presence of the induction periods in the same exchange, might both be attributed to the presence of free iodine in the system. An attempt was made to determine the influence of iodine in the system by preventing the accumulation of iodine. This was done by the addition of the reducing agents, sodium sulfite and sodium thiosulfate. However, in the neutral solution the reducing agents failed to reduce the iodine, and consequently no additional information was obtained on the part played by iodine in the exchange of sodium iodide with o-iodotoluene.

Since there was some free iodine in the reaction mixtures, there was some doubt as to whether true exchange was taking place. The presence of free iodine in equilibrium with the sodium iodide could reduce the specific activity of the sodium iodide indicating an apparent exchange. On the other hand, the active free iodine could possibly substitute into the aromatic compound forming radioactive diiodotoluenes and triiodotoluenes. Consequently, an exchange experiment was done in which the o-iodotoluene was recovered, identified, and counted. The benzene-water technique was used to separate the iodides, following which the benzene layer was carefully evaporated leaving the organic iodide. A portion of this "crude" organic iodide was withdrawn for analysis and the remainder carefully fractionated, the fraction distilling in the range 206 to 208°C being collected for analysis. The separation from diiodo- and triiodotoluenes, if any were present, should have been complete because the melting points for the solid polyiodides range from 30° to 123°C and the boiling points for the liquid polyiodides are all over 295°C. From the results in Table XXX it is apparent that true exchange took place and that no substitution products were formed during the exchange reaction, because the degree of exchange found for the crude material was almost identical with that for the fractionated iodide.

Table XXX. Test for true exchange of o-iodotoluene with sodium iodide.

Experimental conditions	Exchange based on NaI*	Crude RI*	Frac. RI*
0.25 M NaI* 0.75 M RI 71 hr. at 207°C	15.1%	8.3%	8.2%

Since it was apparent that the exchange of o-iodotoluene with sodium iodide was not a "well-behaved" reaction, the exchange of o-iodotoluene with elemental iodine was attempted. The results shown in Table XXXI indicate that exchange was accompanied by substitution of the iodine into the organic compound. This is indicated by the fact that the organic iodide count showed an exchange very much higher than that calculated from the decrease in specific activity of the iodine. Thiosulfate titrations, also reported in Table XXXI, confirmed the loss of free iodine.

Table XXXI. The exchange of 0.50 M o-iodotoluene with 0.10 M iodine.

Conditions	Exchange		$Na_2S_2O_3$ titer
	I_2 anal.	RI anal.	
blank	-----	-----	4.18 ml.
23.5 hr. at 157°C	0%	16%	2.75
23.5 hr. at 185°C	9.2	26	2.86

In summary, the relative rates of exchange of sodium iodide at 210°C with iodobenzene, o-iodotoluene, p-iodobenzoic acid, p-nitroiodobenzene are 1 : 5 : 20 : 250. In addition, o-iodotoluene exchanges at approximately the same rate with iodine as with sodium iodide, but the former exchange is accompanied by substitution of iodine into the organic compound.

DISCUSSION

The availability of the long-lived iodine isotope and the use of severe experimental conditions made it possible to show that various aromatic iodides undergo exchange with sodium iodide. Although numerous investigators have reported that iodobenzene and most other aromatic iodides do not exchange with sodium iodide, positive exchange has been found for iodobenzene, p-iodobenzoic acid, p-nitroiodobenzene, and o-iodotoluene.

Apparently there is a fundamental difference between the exchanges of aromatic and aliphatic iodides with sodium iodide. There is a very marked difference in rate, the rate constant (second order rate constant having units of litres, moles^{-1}, hr.$^{-1}$) of o-iodotoluene at 230°C being about 10^{-2}, while that for butyl iodide at the same temperature is calculated to be about 10^{6}. Also, the exchange of o-iodotoluene is shown to be a complex reaction by induction periods in the reaction-time curves.

In addition, a consideration of the molecular structures in the two classes of iodides shows that exchange of an aromatic iodide with sodium iodide cannot occur by a Walden inversion, the mechanism established for the exchange of aliphatic iodides, because the carbon tetrahedral structure in aliphatic halides does not exist in the aromatic ring. Hence the exchange with aromatic iodides must occur by some other mechanism. The most probable method of exchange involves an approach of the exchanging ion directly to the reaction centre, which is the carbon atom carrying the other iodide atom, leading to the formation of a diiodo transition complex. If so, the exchange rate for a particular aromatic iodide is determined by the ease of approach of the exchanging ion.

Individual differences in aromatic exchange rates may be attributed to the effect of other ring substituents on the charge at the reaction centre, if the steric hindrances are the same in all cases. The nitro group is electronegative with respect to the phenyl group, thus making the molecule a dipole in which, by induction, the carbon atoms of the ring are more positive than they are in the basic member of the aromatic iodides, iodobenzene. In addition, resonance effects in the molecule reduce the negative charge on the carbon atoms ortho and para to the nitro group. Hence, both inductive and resonance effects facilitate the approach of an iodide ion to the reaction centre in the exchange of p-nitroiodobenzene, and consequently exchange occurs more readily than with iodobenzene. The same is true for the exchange of p-iodobenzoic acid, but since the carboxyl group is less electronegative than the nitro group the rate of exchange is less than that of p-nitroiodobenzene.

The methyl group in o-iodotoluene is electropositive with respect to the phenyl group and therefore tends to make the exchange more difficult. At the same time, resonance effects tend to make the carbon atom ortho to the methyl group more positive, hence promoting exchange. Evidently the latter effect predominates, making the exchange rate for o-iodotoluene slightly greater than that for iodobenzene.

The induction period in the reaction-time curves is significant because it indicates that the exchange reaction of sodium iodide with o-iodotoluene is not a simple reaction. The presence of an induction period is usually indicative of an intermediate compound in the reaction. It is possible that elemental iodine is the intermediate in this exchange, but many more experimental data would be required to establish its identity with assurance.

Reaction-time curves for the exchange of diiodotyrosince with potassium iodide showed induction periods for the exchange at low temperatures (38). There was some reason to believe that iodine played an important part in the exchange because free iodine added to the reaction mixture accelerated the reaction considerably. Furthermore, the addition of sodium thiosulfate to the reaction inhibited the exchange, and the exchange of the organic iodide with elemental iodine occurred much faster than the exchange with potassium iodide.

Although diiodotyrosine is an aromatic iodide it appears to be quite different from the aromatic iodides studied in this investigation, and for that reason the diiodotyrosine results probably are not comparable with the results for these aromatic iodides. The most marked difference between diiodotyrosine and iodobenzene, o-iodotoluene, and o-iodobenzoic acid is the rate at which the exchange with alkali iodides occurs. For instance, the exchange of diiodotyrosine in aqueous solution was about 50% complete in one hour at 50°C, when the concentration of the organic iodide was 0.002 M and the potassium iodide 0.00022 M. When the concentrations of the iodides in the exchange of o-iodotoluene with sodium iodide were greater by a factor of about 200, 50% exchange was achieved only after about 80 hr. at 230°C. Hence, the difference between the two classes of compounds is very large. This makes it inadvisable to infer that because the exchange of diiodotyrosine appears to occur through an intermediate exchange with iodine, the same mechanism is responsible for the induction period in the exchange of o-iodotoluene with sodium iodide.

The effect of iodine on the exchanges of sodium iodide with iodobenzene, and p-nitroiodobenzene was studied by Kristjanson (39), and it was found that iodine had no significant effect on the exchange of those compounds. It is somewhat doubtful then, that the induction period in the reaction-time curves in the exchange of sodium iodide with o-iodotoluene was caused by intermediate exchange with iodine.

The induction period might have been caused by the formation of a complex between the organic iodide and sodium iodide, similar to the complexes formed between sodium iodide and various compounds such as acetone, methyl ethyl ketone, and dioxane. The complex would be less stable at higher temperatures, and as a result the induction period would tend to disappear, as was observed at higher temperatures. Also, an increase in the concentration of the organic iodide would effectively lower the concentration of sodium iodide, leading to the reappearance of the induction period, as was observed for the exchange at the highest temperature, 230°C.

In summary, the experimental difficulties encountered in the exchange studies of the aromatic iodides were so great that precise data could not be obtained. The presence of free iodine resulting from thermal decomposition of the organic iodide was an undesirable feature, because it vitiated calculations based on the decrease in the activity of the sodium iodide, and it introduced the possibility of substitution of the iodine directly into the aromatic compound. Since the experimental conditions had to be extreme to allow the exchange to take place, it was difficult to prevent the accumulation of the free iodine.

In view of the facts that it was very difficult to bring about exchange with o-iodotoluene, that the degree of exchange could not be determined with sufficient precision because of the presence of the iodine, and that exchange, when it did occur, was not a simple reaction, the proposed plan of studying the two series of aromatic iodides was abandoned.

Summary and Contribution to Knowledge

A kinetic study has been made of the exchange of radioiodine between butyl iodide and lithium, sodium, caesium, zinc, and cadmium iodides in acetonitrile. A study has also been made of the exchange between butyl iodide and iodine.

The three alkali iodides were shown to be highly ionized in acetonitrile, and since all three exchange at the same rate, the exchange reaction of an alkali iodide with butyl iodide may be regarded as a reaction between butyl iodide and iodide ions:

$$I^{*-} + BuI \rightleftharpoons I^- + BuI^* \quad .$$

The exchanges of the three alkali iodides were characterized by the same activation energy, 18.1 kcal., which was believed to be the activation energy for the exchange of iodide ion with butyl iodide in acetonitrile.

Zinc and cadmium iodides and iodine are only slightly ionized in acetonitrile and the exchange with butyl iodide is slower than the exchange of butyl iodide with the alkali iodides. A comparison of the observed rates with the rate of the alkali iodide exchange, i.e., ion exchange, indicates that butyl iodide exchanges with zinc and cadmium iodides and iodine in the following manner, in which (b) is the rate-determining step:

$$\text{(a)} \quad MI_{n-1}I + I^- \rightleftharpoons MI_n + I^{*-}$$

$$\text{(b)} \quad I^* + BuI \rightleftharpoons I^- + BuI^*$$

There was no indication of direct exchange between butyl iodide and the inorganic molecules.

All exchange reactions, except the exchange of cadmium iodide, were second order. Apparently the cadmium iodide exchange was third order because of the complex nature of the cadmium iodide ionization process.

The activation energies of the zinc and cadmium iodides and iodine exchanges differed from that of the rate-determining step by as much as 3.8 kcal. It was suggested that the differences were essentially the heats of ionization of the inorganic iodides.

It was shown that aromatic iodides, in general, exchange with sodium iodide. The relative rates for the exchange with sodium iodide in acetonitrile are p-nitroiodobenzene > p-iodobenzoic acid > o-iodotoluene > iodobenzene; the relative rates were in accord with the generally accepted theories of induction and resonance in aromatic compounds.

Induction periods observed in reaction-time curves indicated that the exchange reaction of sodium iodide with o-iodotoluene was a complex reaction.

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