[Contribution from The Admiralty, London, England]

# Kinetics of Some Exchange Reactions of the Type RI + $I^{*-} \rightleftarrows RI^* + I^-$ in Alcoholic Solution

### By H. A. C. McKay

The author undertook the research described in this paper in the belief that exchange reactions may eventually play a vital part in the study of reaction kinetics. They represent an unusually simple physicochemical type. The reaction products are chemically identical with the reactants, so the energy diagram of the reacting molecular system must be a completely symmetrical one. There is no heat of reaction to complicate either theory or experiment, only an energy of activation. Moreover, there are no complications due to changes in the chemical composition of the reacting mixture, as the reaction proceeds.

These reactions can be studied by means of radioactive indicators. At the time when the present research was begun, little or no exact work had been done in this field, and it appeared possible to develop a technique which would yield results comparable in accuracy with the general run of reaction kinetics measurements.

The choice of the particular reaction type was made for several reasons. Some preliminary experiments by the author had shown that the speed in alcoholic solution is convenient for measurement[1]; radio-iodine of adequate intensity is readily prepared; and these reactions should be of theoretical interest. On the other hand, the half-life of the radio-iodine used ($I^{128}$) was only twenty-five minutes, a fact which set some novel problems in rapid working.

The accuracy of the measurements is limited, on the physical side, by the accuracy with which it is possible to compare the activities of different samples of radio-iodide. This in turn depends principally on statistical fluctuations in the $\beta$-ray counts. The first problem was thus to obtain activities large enough to reduce the probable statistical error to a low value. With the small amount of radium available (50 mg. in most of the experiments) this could only be achieved by developing a technique based on the Szilard and Chalmers method of concentrating artificial radioelements,[2] as described later. The second problem was to build a measuring instrument capable of handling these activities, and here a Geiger–Müller counter system designed by Wynn-Williams satisfied the author's requirements. The Geiger–Müller counter itself and the measuring vessels were specially designed for handling small quantities of liquids; they are described in a recent paper by the author.[3]

Later developments make a simpler and more accurate technique possible. Eight-day and thirteen-day iodine isotopes have been discovered, and can be prepared at great intensity by means of the cyclotron. If it is ever desired to repeat or extend this work there is, therefore, no reason why the results should not be quite as precise as those of ordinary kinetic studies.

**Analysis of the Kinetics.**—Consider any reaction of the type

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

where $I^*$ is a radio-iodine atom. Let the concentrations of RI and $I^-$ be $a$ and $b$, respectively, and those of $RI^*$ and $I^{*-}$ at a given instant of time $t$ be $x$ and $y$, respectively. Variations in $x$ and $y$ will be due to two causes: the exchange reaction and the radioactive decay. In what follows we will assume that the latter has been corrected for in accordance with the usual exponential formula.

The reaction is followed by comparing the $\beta$-ray intensities of RI samples. These activities are proportional to the fractions of $RI^*$ in the samples, *i. e.*, to $x/a$.

Let the total rate of reaction be $V$. $V$ will be a function of $a$ and $b$, and it will be related to the velocity constant $k$ of the reaction by some equation of the form

$$V = kf(a, b) \qquad (1)$$

The significant point to notice is that $V$ does not vary with $t$, because the *chemical* composition of the reacting mixture is constant.

An $RI^*$ molecule is formed whenever an RI molecule reacts with an $I^{*-}$ ion. $I^{*-}$ ions form a fraction $y/b$ of the total number of $I^-$ ($+ I^{*-}$) ions, so that on simple probability grounds, $RI^*$

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(1) McKay, *Nature*, **139**, 283 (1937).

(2) Szilard and Chalmers, *ibid.*, **134**, 462 (1934).

(3) McKay, *Rev. Sci. Inst.*, **12**, 103 (1941).

is formed at a rate $yV/b$. Similarly it is lost in the reverse reaction at a rate $xV/a$. Thus

$$dx/dt = (-x/a + y/b)V$$

A similar equation holds for $I^{*-}$

$$dy/dt = (x/a - y/b)V$$

If all the activity is initially present as $I^{*-}$, we have $x = 0$ when $t = 0$; this corresponds to the author's actual experimental conditions. Integration of the equation then gives

$$-\log_e(1 - x/x_\infty) = V(a + b)t/ab \qquad (2)$$

where $x_\infty$ is the limiting value of $x$ when exchange is complete, *i. e.*, at $t = \infty$. It will be seen that a plot of $x/x_\infty$ against $t$ is independent of the form of $V$.

By changing $a$ and $b$ we can of course determine the form of the function f in (1); this includes a determination of the order of the reaction. If our exchange is a simple bimolecular reaction, as we expect, we shall have

$$V = kab$$

$$-\log_e(1 - x/x_\infty) = k(a + b)t \qquad (3)$$

It is to be emphasized that equation (2) is an exact one, irrespective of deviations from the laws of ideal solutions, and would only fail to hold exactly if $x$ and $y$ became commensurate with $a$ and $b$. The cause of any (apparent) deviation from (2) must, therefore, be sought in the experimental technique, or in the failure of our initial assumption that we are dealing with a single homogeneous reaction. The latter possibility appears unlikely. It was demonstrated that there is no appreciable heterogeneous reaction in the exchanges here investigated; side reactions do not usually occur to any great extent; and though a simultaneous reaction with an impurity is possible, such impurity would have to be present in impossibly large amount to affect the validity of (2) at all seriously.

## Experimental

The rate of the exchange reaction was measured by adding an alcoholic solution of sodium radio-iodide to the inactive alkyl iodide. At suitable times, samples were removed and the alkyl iodide separated off; one sample was heated sufficiently to take the exchange to completion. The activities of the alkyl iodide samples were compared by means of the Geiger–Müller counter, and the values of $x/x_\infty$ so found were inserted in equation (3) to give $k$.

**Preparation of the Sodium Radio-iodide Solution.**—The Szilard and Chalmers method of concentrating radioiodine is to activate a substance like ethyl iodide, when some 50% of the active atoms appear as a trace of free iodine.[2] The activity is separated by shaking the ethyl iodide with a suitable aqueous solution and then precipitating silver radio-iodide.

The author, who required the radio-iodine as sodium radio-iodide in alcoholic solution, had to work out a more complicated technique. A rapid method was essential, on account of the short life of $I^{128}$, and this ruled out many of the ordinary operations of chemistry, such as the evaporation of an aqueous solution. The technique finally evolved enables sodium radio-iodide to be prepared within ten minutes of the end of the activation.

(1) 200–300 cc. of ethyl iodide, in which a small crystal of iodine has been dissolved, is activated in a paraffin block for at least an hour. The trace of free iodine acts as a carrier for the radio-iodine set free.

(2) The activated material is shaken with 10–15 cc. of water containing a little dissolved sulfur dioxide. In this process the iodine is reduced and goes into the aqueous layer. The ethyl iodide is run off and dried with calcium chloride, so as to be ready for use in a fresh activation.

(3) The aqueous layer from (2) is poured into a small separating funnel containing 3–4 cc. of methylene chloride. Concentrated nitric acid is added to set free the iodine, which goes into the methylene chloride on shaking.

(4) The methylene chloride layer is run off and evaporated nearly to dryness. Then 1–2 cc. of alcohol is added, and the evaporation is continued. In this two-stage process, the methylene chloride, chosen on account of its volatility, can be removed completely without loss of iodine. We are left with a trace of radio-iodine dissolved in a small volume of alcohol.

(5) Sodium iodide solution containing a known amount of sodium iodide is added to the radio-iodine solution. The mixture is brought to boiling for a moment. Exchange takes place, and as there is normally much more sodium iodide than iodine present, nearly all the activity goes into the iodide.

(6) It only remains to remove the small amount of iodine from the solution. This is done by boiling up with a piece of copper gauze, which has been reduced by dipping it red hot into methyl alcohol. Finally the gauze is removed and any sodium iodide adhering to it is washed back into the solution. The solution is made up to a known volume ready for adding to the reaction mixture.

**The Exchange Reaction.**—The reaction is carried out in a thin-walled glass bulb in a thermostat. The alkyl iodide and as much alcohol as is required are placed in this bulb and allowed to come to the right temperature; in some cases inactive sodium iodide is added to this mixture as well. The active sodium iodide solution, of known volume and concentration, is brought to a temperature a degree or two above that of the thermostat, and then run into the center of the bulb by means of a thistle funnel. A bubble or two of air is blown down the funnel to ensure rapid mixing.

One sample is immediately pipetted out for use as an "infinity" sample. It is run into a strong glass tube, sealed off, and then heated to 80–100° for long enough to take the exchange reaction to within at least 0.5% of completion. The heating must not be unnecessarily prolonged, or side-reactions set in liberating iodine.

At suitable time intervals three further samples are removed. The times are chosen so that activities of the alkyl iodide in the samples are roughly in the ratios 0.3: 0.5:0.75:1, the last being the infinity sample. With the technique used it is unnecessary to bother about the exact volumes of the samples.[3]

**Separation of the Alkyl iodide.**—The original idea was to separate off the alkyl iodide by pouring the reaction samples into water. Later three substances were added to the water to improve the separation:

(1) **Sodium iodide** is very important. In its absence much of the alkyl iodide is lost in the form of a powdery-looking quasi-emulsion.

(2) **Sulfur dioxide** serves to remove accidental traces of free iodine which might otherwise get absorbed on the cellophane windows of the measuring vessels.

(3) **Magnesium chloride** has a strong salting-out effect, and is added to improve the yield of precipitated alkyl iodide.

The separation is carried out in a special vessel designed to minimize loss of the small volume of alkyl iodide involved (about 0.5 cc.). This vessel contains the solution just described, the volume chosen being about double that of the reaction sample to be dealt with; this quantity gives the best yield. After the iodide has been precipitated, the aqueous layer is sucked off, and the iodide washed with distilled water. Finally the lower layer is run off into one of the measuring vessels; if desired it can be dried by means of a small crystal of calcium chloride, though this seems to have no effect on the readings.

**The Activity Readings.**—The highest accuracy with a Geiger–Müller counter is obtained when the samples compared are of approximately equal activity. This is readily achieved with the short-lived radio-iodine by measuring the least active sample first and then the more active ones after they have had time to decay. The activities, as already mentioned, were roughly in the ratios 0.3:0.5: 0.75:1, so with a 25-min. period approximately equal counts were obtained by measuring the successive samples for ten minutes each.

The counter could not deal accurately with speeds higher than 400/min. Whenever this speed was exceeded, the readings were reduced by means of "stops" of various sizes: these consisted of annular brass rings, about 1.5 mm. thick, placed between the measuring vessel and the counter.

**Range of the Experiments.**—The short half-life of $I^{128}$ places a fairly sharp limit to the length of the experiments. Every factor of two in the initial intensity of the radio-iodine adds twenty-five minutes to the available working time, and on the other hand every 10° lowering of the temperature more than doubles the time required. The strongest neutron source available to the author (about 300 millicuries) gave a working time of about two hours up to the removal of the final reaction sample for analysis and measurement. To go 10° lower would mean a working time over two hours longer, *i. e.*, at least five $I^{128}$ half-periods; this would necessitate a source of about 10 curies.

At the other end of the scale, it is hardly possible to remove the first reaction sample before two to three minutes have elapsed, which means that the last sample will probably be removed after ten minutes. This gives a total factor of perhaps 15 in the reaction velocities which can be measured, corresponding to a temperature range of 25 to 30°.

The range of alkyl iodide concentrations is determined by the necessity of recovering the alkyl iodide for measurement, and a factor of just over 4 is available. There are no obvious limits apart from solubility to the sodium iodide concentrations, and a range of nearly 100:1 was in fact used.

## Results

**Test of the Technique.**—Methyl iodide comes to exchange equilibrium very rapidly, and once equilibrium has been reached, a series of successive methyl iodide samples should all show the same activity. In an experiment of this kind, the activities of four successive samples, after all the usual corrections had been made, were

| | | | |
|---|---|---|---|
| First sample | 1132 | Third sample | 1181 |
| Second sample | 1179 | Fourth sample | 1179 |

The divergence of the first sample from the others is scarcely greater than the probable statistical error, and may in any case be due to the reaction not being quite complete. The agreement is therefore very satisfactory.

**Accuracy of the Results.**—59 runs were made, and the results are recorded in Tables I and II. Each $k$-value (except that for $t$-BuI) is the mean of three readings corresponding to three $x/x_\infty$ values. To give some idea of the agreement, standard errors have been calculated by the usual formula.

The statistical error in a single $x/x_\infty$ value is usually about 4%. This becomes somewhat magnified in calculating $k$, the more so the larger $x/x_\infty$. If the values of $x/x_\infty$ for the three samples are 0.3, 0.5 and 0.75, then the 4% error becomes magnified to 5, 6 and 9%, respectively.

There may also be errors in timing, in mixing the reactants, and in the temperature of the mixture. These sources of error will be greatest for the first sample and least for the last. We shall therefore probably not be far wrong in putting a round 10% on the error in each individual $k$-value, and 5% on the final $k$-value.

Often, however, the experimental divergences are greater. The standard error sometimes exceeds 10% of the mean. And when there is a big divergence it is always in one direction: the $k$-values tend to decrease from the first to the third sample. The reason for this was not discovered, but as the effect was fairly consistent it is to be hoped that although it may affect the absolute values of $k$ it will not greatly affect the comparative mean values.

TABLE I

VELOCITY CONSTANT OF THE EXCHANGE REACTION OF EtI

Temperature, 30°C.

| EtI $N$ | NaI $N$ | $k \times 10^3$ (l./mol. sec.) | EtI $N$ | NaI $N$ | $k \times 10^3$ (l./mol. sec.) |
|---|---|---|---|---|---|
| 0.90 | 1.52 | 0.220 ± 0.012 | 2.0 | 0.60 | 0.246 ± 0.017 |
| .90 | 1.10 | .221 ± .005 | 3.0 | .60 | .227 ± .008 |
| .91 | 0.60 | .258 ± .021 | 3.5 | .60 | .217 ± .007 |
| .91 | .33 | .308 ± .019 | 4.01 | .60 | .189 ± .013 |
| .91 | .135 | .337 ± .036 | 4.01 | .44 | .236 ± .007 |
| .91 | .135 | .327 ± .026 | 4.01 | .29 | .258 ± .021 |
| .95 | .068 | .346 ± .031 | 4.01 | .15 | .281 ± .019 |
| .90 | .033 | .421 ± .047 | 4.01 | .075 | .340 ± .030 |
| .92 | .017 | .425 ± .057 | 4.01 | .030 | .443 ± .033 |

TABLE II

VELOCITY CONSTANTS OF THE EXCHANGE REACTIONS OF ALKYL IODIDES AT VARIOUS TEMPERATURES

| Temp., °C. | $k \times 10^3$ (l./mol. sec.) |
|---|---|
| EtI<br>EtI, 0.91 $N$; NaI, 0.135 $N$ | |
| 20 | 0.108 ± 0.006 |
| 25 | .174 ± .006 |
| 30 | .332 ± .020 |
| 35 | .569 ± .012 |
| 40 | .899 ± .041 |
| 45 | 1.37 ± .05 |
| 50 | 3.20 ± .18 |
| PrI<br>PrI, 0.75 $N$; NaI, 0.135 $N$. | |
| 35 | 0.374 ± 0.007 |
| 45 | .938 ± .024 |
| 55 | 2.35 ± .00 |
| *i*-PrI<br>*i*-PrI, 1.62 $N$; NaI, 0.142 $N$ | |
| 45 | 0.0635 ± 0.0043 |
| 50 | .0994 ± .0040 |
| 55 | .104 ± .008 |
| 60 | .262 ± .013 |
| 65 | .426 ± .026 |
| 70 | .698 ± .063 |
| BuI<br>BuI, 0.64 $N$; NaI, 0.135 $N$ | |
| 30 | 0.165 ± 0.009 |
| 35 | .275 ± .008 |
| 40 | .439 ± .021 |
| 45 | .690 ± .050 |
| 50 | 1.09 ± .03 |
| 55 | 1.75 ± .03 |
| 60.5 | 2.85 ± .08 |

| Temp., °C. | $k \times 10^3$ (l./mol. sec.) |
|---|---|
| *i*-BuI<br>*i*-BuI, 1.42 $N$; NaI, 0.142 $N$ | |
| 40 | 0.0587 ± 0.0043 |
| 45 | .0931 ± .0091 |
| 50 | .150 ± .017 |
| 55 | .231 ± .034 |
| 60 | .354 ± .053 |
| 65 | .534 ± .068 |
| 70 | .848 ± .098 |
| *s*-BuI<br>*s*-BuI, 1.42 $N$; NaI, 0.142 $N$ | |
| 45 | 0.0705 ± 0.0065 |
| 50 | .122 ± .007 |
| 55 | .192 ± .006 |
| 60 | .324 ± .025 |
| 65 | .567 ± .014 |
| 70 | .882 ± .043 |
| *t*-BuI<br>*t*-BuI, 1.24 $N$; NaI, 0.37 $N$ | |
| 40 | 0.94 (no infinity sample) |
| AmI<br>AmI, 0.56 $N$; NaI, 0.135 $N$ | |
| 40 | 0.530 ± 0.020 |
| 50 | 1.36 ± .02 |
| 60.5 | 3.56 ± .13 |
| *i*-AmI<br>*i*-AmI, 0.715 $N$; NaI, 0.137 $N$ | |
| 50 | 0.572 ± 0.033 |
| $CH_2I_2$<br>$CH_2I_2$, 0.48 $N$; NaI, 0.06 $N$ | |
| 60 | 1.036 ± 0.022 |

**Effect of Concentration Changes.**—As we have seen, the only means of determining the order of the reaction is by varying the concentrations of the reactants. It is probable that most alkyl iodides behave similarly with respect to concentration variations, so these experiments were confined to ethyl iodide at 30°.

Three series of experiments were made. In the first two series the ethyl iodide concentration was kept constant or nearly so, at 0.91 and 4.00 $M$ and the sodium iodide concentration was varied. In the third series of experiments the ethyl iodide concentration was changed.

These results demonstrate that the reaction is bimolecular. A 100-fold variation in the concentration of the sodium iodide produces only a 2-fold change in the bimolecular velocity constant; and a 4-fold change in the ethyl iodide concentration produces only a 20% change. These residual variations in $k$ are, of course, due to deviations from ideality of the solution. As an empirical result it was found that the velocity constant plotted against the logarithm of the sodium iodide concentration gave a rough straight line, but this relation must clearly break down at the lowest concentrations.

**Temperature Coefficients.**—Quite good straight lines were obtained on plotting log $k$ against $1/T$ (though the figure for EtI at 50° unaccountably deviates), and from the slopes of these lines the energies of activation were calculated for the different compounds studied. Small but undoubtedly significant differences were found between the primary and secondary compounds: (1) primary iodides (containing a $CH_2I-$ group) have an activation energy of 19 kcal. These include ethyl, propyl, butyl, isobutyl and amyl iodides.

(2) Secondary iodides (containing a $CHI<$ group) have an activation energy of 20.5 kcal. These include isopropyl and *s*-butyl iodides.

**Absolute Rates.**—The differences in the absolute rates are also of interest. We observe that (1) among the primary straight-chain iodides, the rate falls from methyl (which reacts very rapidly) through ethyl and propyl to butyl, and rises again to amyl iodide. (2) Branching in the chain reduces the rate by a considerable factor (*cf.* butyl and isobutyl iodides, amyl and isoamyl iodides). (3) The rate falls in the series $CH_3I$, $CH_2MeI$, $CHMe_2I$, but rises again to $CMe_3I$. Probably the crowding of the central carbon atom in $CMe_3I$ is so great as to render the compound rather unstable. (4) The introduction of a second iodine atom causes a much bigger diminution in the rate than the introduction of a methyl group (there is a much greater fall from $CH_3I$ to $CH_2I_2$ than from $CH_3I$ to $C_2H_5I$).

## Summary

A technique has been worked out for the study

of the kinetics of the exchange reactions between alkyl iodides and iodide ions in alcoholic solution, using $I^{128}$ as an indicator. A new method of obtaining $I^{128}$ in concentrated form, and special measuring apparatus were required. Novel problems in rapid working were set by the short period (25 mins.) of $I^{128}$.

The following results were obtained: (1) The reactions are bimolecular. (2) The dependence of the bimolecular velocity constant on the concentrations of the reactants was determined for ethyl iodide at 30°. (3) The velocity constants and their temperature coefficients were determined for a series of alkyl iodides.

(4) The publication of this manuscript has been unavoidably delayed by the loss of mail in transit.—*The Editor.*

RECEIVED MARCH 7, 1942[4]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

# On the Kinetics of Polymerization Reactions. I. First Order Initiation Reaction[1]

BY ROBERT GINELL AND ROBERT SIMHA[2]

It is generally accepted today that there are essentially two types of polyreactions leading to the formation of polymers, namely, polycondensation processes, and polymerization reactions in a more restricted sense. The first is a step reaction consisting of a step-wise addition (accompanied by the removal of, *e. g.*, a water molecule) of monomer or polymer. Polymerization reactions on the other hand are processes involving several elementary reactions. Due to the efforts of several workers[3] it has been established that generally four elementary acts must be considered in a chain polymerization. First, an initiation reaction, leading to the activation of a stable monomer molecule of the polymerizable material. Second, a growth reaction of the activated nuclei, creating more or less large molecules. Third, a stabilization reaction of the growing particles. Finally the possibility must be admitted that a chain molecule is able to grow in two or more directions, thus leading to branched molecules. The particular mechanisms involved in these elementary steps, especially in the fourth one, have not as yet been completely clarified for actual polymerizable substances, like styrene or methyl methacrylate, under various experimental conditions as photo-polymerization, thermal activation or catalytic polymerization. However, it appears possible to derive on general grounds certain elementary relationships between the individual rates and the characteristic kinetic quantities like total rate of polymerization, change of average molecular weight and the molecular weight distribution during the course of the reaction. The rates can also be correlated with the properties of the final product.

The kinetic processes discussed above as well as the inverse one, the depolymerization of chain molecules, can be treated in principle by two methods, a deterministic and a statistical one.[4] In the first one, rate equations are formulated for the respective process, usually in the form of differential equations containing the time, *t*, as independent variable, and the concentrations of the various species appearing during the course of the reaction as dependent ones. On the other hand, in processes involving a large number of individual acts, as in radioactive disintegrations, chain and step reactions leading to the union of a relatively large number of reacting partners, a statistical approach to the problem can be chosen. The results so obtained for the relative occurrence of each species are usually expressed, in terms of one or more parameters, the significance of which follows from the nature of the respective problem. An additional consideration, similar to that employed in the first method, gives then the dependence of these parameters upon time.

The first type of approach for simple consecutive reactions was developed principally by Rak-

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(1) Presented at the One Hundred Fourth meeting of the American Chemical Society held in Buffalo, New York, September 7-11, 1942.

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(3) For references see R. E. Burk, A. J. Weith, H. E. Thompson and I. Williams, "Polymerization, and its Applications in the Fields of Rubber, Synthetic Resins and Petroleum," Reinhold Publishing Company, " New York, N. Y., 1937; and H. Mark and R. Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941.

(4) A general discussion of some aspects of these methods and their application to radioactive and other processes has been recently given by I. Opatowski, *Proc. Nat. Acad. Sci.*, **28**, 83 (1942).