The Isotopic Exchange Reaction

This experiment has been designed to illustrate the use of radiotracers in studies of chemical reaction kinetics. The particular experiment to be performed is a classical one (1) and involves the exchange of ^{131}I ions from sodium iodide with iodine atoms in n-~~butge~~ butyl iodide.

A. SURVEY OF PROBLEM

When a radioactive atom in one chemical state is added to a mixture of nonradioactive atoms of the same element, one frequently observes that some of the radioactive atoms will replace the stable atoms in the mixture or compound, etc. Such a process is called an "exchange reaction". Such reactions are important because of their use in labeling atoms in a compound and the fact that the unwanted occurrence of such processes can negate many tracer studies. In addition, exchange reactions are simple, interesting reactions that illustrate many of the fundamental principles of chemical kinetics.

Consider an exchange reaction of the type

$$AX^* + BX \rightleftharpoons AX + BX^* \qquad \text{(I-1)}$$

where X^* represents a radioactive X atom. Let the rate of reaction (i.e., the total number of all possible exchanges per second) be R mole/l -sec.

Further define

concentration of $AX^* \equiv x$ mole/l .

concentration of $BX^* \equiv y$ mole/l .

concentration of $X^* \equiv x + y \equiv a$ mole/l . (I-2)

concentration of $(AX^* + AX) \equiv b$ mole/l .

concentration of $(BX^* + BX) \equiv C$ mole/l .

Note that b is the total concentration of AX molecules, i.e., labeled and unlabeled while C is the total concentration of BX molecules, labeled and unlabeled. The rate of formation of AX^* is the reaction rate (R) times the fraction of the reactions that occur with an active BX^* $(\frac{y}{C})$ times the fraction of reactions that occur involving inactive AX $(\frac{b-x}{b})$. In other words, the rate of formation of AX^* is $\frac{Ry}{C}\left(\frac{b-x}{b}\right)$. Similarly, the rate of destruction of AX^* is $R\frac{x}{b}\left(\frac{c-y}{c}\right)$. Thus the total rate of change of the concentration of AX^* per unit time is given as the rate of formation minus the rate of destruction, i.e.,

$$\frac{dx}{dt} = \frac{Ry}{C}\left(\frac{b-x}{b}\right) - \frac{Rx}{b}\left(\frac{c-y}{c}\right) \qquad \text{(I-3)}$$

$$\frac{dx}{dt} = R\left(\frac{y}{c} - \frac{x}{b}\right) \qquad \text{(I-4)}$$

Assume that at t=0, x=0, i.e., all the active material is added to the system in the form of BX^*. At $t = \infty$, complete equilibrium will occur, i.e., the exchange will be complete. Then the specific activities of AX and BX will be equal. In other words

$$\frac{x_\infty}{b} = \frac{y_\infty}{c} \qquad \text{(I-5)}$$

But remember, the specific activity must be $\frac{a}{b+c}$, i.e., the total concentration of active species divided by the concentration of inactive species. Thus

$$\frac{x_\infty}{b} = \frac{a}{b+c} = \frac{y_\infty}{c} \qquad \text{(I-6)}$$

Using equation I-2 for the definition of a, we have

$$\frac{x_\infty}{b} = \frac{x+y}{b+c} \qquad \text{(I-7)}$$

In other words

$$y = x_\infty \left(\frac{b+c}{b} \right) - x \qquad \text{(I-8)}$$

If we now integrate equation I-4, we perform the following steps

$$\frac{dx}{dt} = R \left(\frac{y}{c} - \frac{x}{b} \right) \qquad \text{(I-9)}$$

$$\frac{dx}{dt} = R \left(\frac{x_\infty (b+c)}{bc} - \frac{x}{c} - \frac{x}{b} \right) \qquad \text{(I-10)}$$

$$\frac{dx}{x_\infty - x} = \left(\frac{b+c}{bc} \right) Rdt \qquad \text{(I-11)}$$

$$\int \frac{dx}{x_\infty - x} = \int \frac{b+c}{bc} Rdt \qquad \text{(I-12)}$$

$$-\ln\left(1 - \frac{x}{x_\infty}\right) + C = \frac{b+c}{bc} Rt \qquad \text{(I-13)}$$

where C is the integration constant. We can evaluate C by remembering [redacted] Thus C=0 and we have

$$-\ln\left(1 - \frac{x}{x_\infty}\right) = \frac{b+c}{bc} Rt \qquad \text{(I-14)}$$

Note therefore, that a plot of ln $\left(1- \frac{x}{x_\infty}\right)$ vs t will give the reaction rate R independent of any assumption about the reaction mechanism.

The half time, $t_{1/2}$, for the exchange is the time it takes for $\frac{x}{x_\infty}$ to equal 1/2. Thus, substituting in equation I-14 the value of 1/2 for x/x_∞, we get

$$t_{1/2} = \frac{0.693\ bc}{(b+c)\ R} \qquad \text{(I-15)}$$

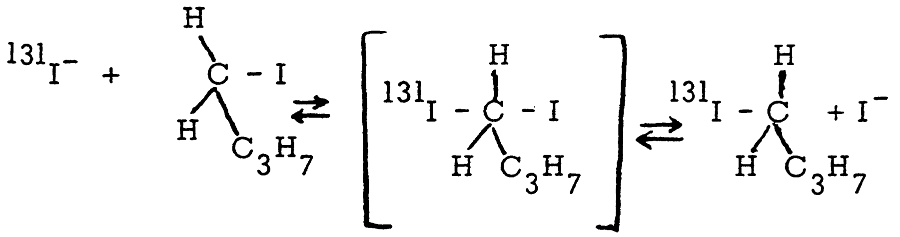
Half-times for exchange reactions can vary from fractions of a second to years.

B. SPECIFIC EXPERIMENTAL PLANS

The equations derived in Section A of this experiment apply to any exchange reaction regardless of reaction mechanism. For the specific exchange reaction we are to study

$$\text{NaI} + C_4H_9{}^{131}\text{I} \rightleftarrows \text{Na}^{131}\text{I} + C_4H_9\text{I} \qquad \text{(I-16)}$$

the reaction mechanism is bimolecular. In fact, this reaction is said to be a classic example of an SN2 reaction, involving an unstable transition state between the iodide ion and the alkyl iodide. Specifically, the reaction takes place by means of a Walden inversion, i.e.,



(I-17)

The expression for the reaction rate R for a bimolecular reaction can be written as

$$R = kbc \qquad \text{(I-18)}$$

where k is called the rate constant. Thus by substituting into equation I-15, we can get an expression for k, i.e.,

$$k = \frac{0.693}{(b+c)\, t_{1/2}} \qquad \text{(I-19)}$$

If the exchange reaction is carried out at two different temperatures, one can use the Arrhenius equation to derive a value of the activation energy, ΔE, for the reaction, i.e., the minimum energy which one molecule must possess in order to react with one another. Specifically,

$$\Delta E = 2.303\, R \frac{T_2 T_1}{T_2 - T_1} \log_{10} \frac{k_2}{k_1} \qquad \text{(I-20)}$$

where R is the universal gas constant (1.98 cal/^{o}K-mole) T_1, T_2 are the two temperatures (^{o}K) of the reaction systems in which rate constants k_1 and k_2 were measured.

C. EXPERIMENTAL PROCEDURE*

1. Place ten 15 ml centrifuge tubes in a beaker filled with ice and add 5 ml 0.06 M NaI aqueous solution and 5 ml benzene. Set aside these tubes for future use.

2. Prepare 10 ml of a 0.06M NaI solution in 90% acetone containing ~ 20,000 cpm ^{131}I and at the same time prepare a solution of 0.06 M n-butyl iodide in 90% acetone. Place the NaI solution and the n-butyl iodide solution in a constant temperature bath (t = 45 $\pm$ 1^{o}C) and let the flasks equilibrate.

3. Mix the two solutions thoroughly by taking 5 ml of each solution and adding it to a 15 ml test tube, keeping the temperature constant at 45 $\pm$ 1^{o}C. Shake each mixture for 1-2 minutes. Record this time, t_o.

   t_o = ________________.

4. Every 10 minutes withdraw a 500 μl aliquot of the reaction mixture and add it with thorough mixing to one of the previously prepared centrifuge tubes. This "quenches" the exchange, i.e., reduces the reaction rate drastically. Centrifuge this tube until the two layers separate and remove all the top (benzene) layer with a pipet into a 2 dram poly-vial. Seal the vial. Transfer the aqueous layer to a separate two dram

*The experimental procedure described herein is a modification of one described in R. T. Overman and H. M. Clark, Radioisotope Techniques (McGraw-Hill, New York, 1960).

vial, and seal it. The benzene layer will contain the n-butyl iodide while the aqueous layer will contain the NaI. Take 10 samples at 10 minute intervals.

5. Count all samples with a 3" x 3" NaI (Tl) well-type scintillation counter. Record the background corrected counting data in Table I-1.

6. Repeat the experiment using a reaction temperature of $25 \pm 1^{o}C$ and sampling intervals of ten minutes. (Or alternatively, divide the original group doing the experiment into two groups with each group working at a different temperature). Record the $25^{o}C$ data in Table I-2.

7. Plot $-\log_{10}\left(1-\frac{x}{x_\infty}\right)$ vs. time of sampling using semilog paper. The value of x_∞ used should be the average value of x_∞ values determined in each measurement. As shown in equations I-14 and I-18, the above plot should give a straight line with slope k, the rate constant, where k is $R\left(\frac{b+c}{bc}\right)\frac{1}{2.303}$. Calculate k and R for each temperature.

	$25^{o}C$	$45^{o}C$
k	______	______
R	______	______

8. Calculate the half life of the reaction, $t_{1/2}$, at each temperature using equation I-15.

	$25^{o}C$	$45^{o}C$
$t_{1/2}$	______	______

9. Using equation I-20, calculate the activation energy, ΔE, for the reaction ΔE = ____________

Table I-1

$T = \_\_\_\ ^{o}K$

Sample Number	Time of Sampling	Benzene Layer Activity, x	Aqueous Layer Activity	x_∞
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

x_∞ (average) = ________

$$x_\infty = \frac{\text{Benzene layer activity} + \text{Aqueous layer activity}}{2}$$

Table I-2

$T = \_\_\_\ ^{o}K$

Sample Number	Time of Sampling	Benzene Layer Activity, x	Aqueous Layer Activity	x_∞
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

x_∞ (average) = ________