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KINETICS OF TRITIUM REMOVAL FROM HEAVY WATER
BY EXCHANGE WITH DEUTEROCHLOROFORM

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ABSTRACT

A technique was developed to determine the rate and equilibrium constants for the base-catalyzed exchange of tritium from heavy water to deuteriochloroform. An activation energy and entropy were also calculated. These quantities are comparable with those reported in the literature for a similar reaction involving the exchange of deuterium from deuteriochloroform to water. It was found that the exchange reaction occurred predominately between the dissolved reactants in the D_2O and $CDCl_3$ phases. The rate constant is a strong direct function of temperature while the equilibrium constant is a weak inverse function.

INTRODUCTION

The handling and processing of tritiated heavy water poses severe environmental hazards. Present methods of tritium removal from heavy water lead to a concentrated liquid tritium waste product which is difficult and expensive to dispose of. Cost estimates for such a process indicate that the system would be prohibitively expensive, with a major portion of the capital investment directly attributable to the cost of process liquid containment (1).

An alternative has been proposed by I. P. Herman and J. B. Marling (2) which involves the transfer of tritium from heavy water to a deuteriochloroform carrier molecule in the presence of NaOD:

Water and chloroform are relatively insoluble. The reaction, therefore, takes place at the interface between the two phases, and within each phase using the small amounts of dissolved reactants. The tritiated chloroform is then

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dissociated by an isotopically-selective infrared laser, after which the greatest fraction of tritium will exist as TCl. Present plans call for the TCl to be absorbed onto a solid and then disposed of or processed for tritium recovery.

This paper is a report of summer work performed to determine the rate and equilibrium constants of Equation (1) over a variety of temperatures and hydroxide concentrations. An activation energy was also determined. Briefly, the exchange reaction was performed by the addition of NaOD to a stirred vessel containing DTO/D₂O and CDCl₃. Samples of each phase were removed from the reaction mixture at recorded time intervals, and analyzed for tritium content by liquid scintillation counting.

An estimate using statistical mechanics indicates that the equilibrium constant is approximately 0.5 at room temperature (3). The rate constant may be estimated from data by Hine, Peek and Oakes concerning the deuterium exchange of dissolved chloroform in aqueous solution (4). A summary of these data is presented in Table I, which will be used in the Results section for comparison.

TABLE I - Selected Kinetic Data of Hine, Peek and Oakes on the Base-Catalyzed Exchange of Dissolved Chloroform* in Aqueous Solution (4).

$\text{CDCl}_3 + \text{H}_2\text{O} \xrightarrow[k_1]{\text{NaOH}} \text{CHCl}_3 + \text{HOD}$		
Temperature (°C)	100k ₁ (M ⁻¹ sec ⁻¹)	
0.0	0.470 ± 0.01	
20.1	10.2 ± 0.2	
35.0	73.5 ± 1.0	

Temperature Range (°C)	Heat of Activation (kcal/mole)	Entropy of Activation (cal/mole °K)
0 - 20.1	23.8	18.2
20.1 - 35.0	23.2	16.1

*All CDCl₃ is dissolved in H₂O

EXPERIMENTAL

The kinetic runs were made by a procedure of which the following point is an example. 30.0 ± 0.2 ml of CDCl_3 (Aldrich 15,182-3, 99.8 atom %) was mixed with 30.0 ± 0.2 ml of a 11.5 ± 0.5 $\mu\text{Ci/cc}$ DTO in D_2O solution (D_2O stock from Aldrich 15,188-2, 99.8 atom %) in a closed four-neck 100 ml flask immersed in a 25.0 ± 0.2 $^\circ\text{C}$ bath. The flask also contained a Teflon[®] stirring blade on a glass shaft, a cooling coil column, a thermometer and a sampling port. Use of the cooling coil allowed the experiment to be performed at constant pressure in a closed system and reduced the loss of reactants due to evaporation. After the reactants were allowed to thermally equilibrate, 0.5 ml samples of both the D_2O and the CDCl_3 phases were taken with an Eppendorf automatic pipetter. The reaction was started by injecting 1.00 ± 0.01 ml of 0.617 M NaOD (NaOD stock Aldrich 17,678-8, 40 wt. % solution in D_2O) into the flask and starting the stirring motor, which rotated at 860 rpm. Since the exchange reaction does not proceed to any appreciable extent without the presence of a base catalyst, the reaction can be precisely started by addition of base and quenched by addition of acid.

Approximately 0.5 ml samples of each phase were taken at five minute intervals for the first half-hour of the reaction, with subsequent samples taken at progressively longer intervals. Each sample was placed in a separate vial containing 0.100 ± 0.002 ml of 4.06 M HCl, which is approximately twice the required amount needed to quench the reaction. The 40-second time interval in which the stirring motor was stopped to take a sample was not counted in the reaction time for the higher-rate runs (six, seven and eight).

The next step was to remove any remaining tritiated compounds which were dissolved in the bulk phases. More than 99 mole percent of the dissolved DTO was extracted from the CDCl_3 samples by adding 15 ml of H_2O to each sample and mixing in an ultrasonic bath for five minutes. The same technique was applied to extract dissolved CTCl_3 from D_2O samples by adding 10 ml of CS_2 . Later runs utilized CHCl_3 to extract CTCl_3 from the D_2O samples. Using both techniques, more than 94 mole % of the dissolved CTCl_3 was extracted from the D_2O samples.

Duplicate $0.020 \pm .0002$ ml aliquots of all samples were taken with glass micropipets, mixed with 15.0 ± 0.1 ml of liquid scintillation cocktail (Insta-Gel, United Technologies-Packard) and counted for tritium content in a Packard Tri-Carb 460C Liquid Scintillation System, using calibration curves prepared by J. Maienschein. Three six-minute counts were made of each aliquot and then averaged. These counts often differed by as much as one percent, with the greater deviations occurring at higher tritium concentrations. The background counts measured in pure scintillation cocktail were subtracted from the sample counts. Where wide differences between counts of duplicate aliquots were produced, a third aliquot was obtained and counted.

The CTCl_3 counts were used to compute the instantaneous concentration of CTCl_3 at specific times in the reaction, from which equilibrium and rate data were derived. The DTO data was unreliable since the concentration of DTO changed very little when equal volumes of tritiated D_2O and CDCl_3 were reacted. The small change in concentration was masked by errors in counting and pipetting, so the DTO samples were only used for a rough tritium balance to check the general accuracy of the measured CTCl_3 concentrations.

RESULTS AND DISCUSSIONS

The proposed mechanism for the base catalyzed exchange of tritium from heavy water to deuteriochloroform is

with the formation of the chloroform ion being the slow step (4). The rate of formation of CTCl_3 can be expressed as

$$\frac{d [\text{CTCl}_3]}{dt} = k_2 [\text{CCl}_3^-] [\text{OTO}] - k_{-2} [\text{CTCl}_3] [\text{OD}^-] \quad (4)$$

Using the steady state approximation on $[\text{OD}^-]$ and introducing the equilibrium constant, we obtain

$$\frac{d [\text{CTCl}_3]}{dt} = k_{-2} [\text{OD}^-] \left(K_{\text{eq}} [\text{CDCl}_3] \frac{[\text{OTO}]}{[\text{D}_2\text{O}]} - [\text{CTCl}_3] \right) \quad (5)$$

Two assumptions were made here: first, that essentially the entire reaction occurs in the dissolved portions of each phase within the other, and that any interfacial tritium transfer could be neglected; and second, that the dissolved reactants exchange quickly and completely with the bulk phases so that the concentrations and characteristics of the dissolved reactants are in every way identical to the bulk.

Following a derivation by Maienschein we obtain

$$\frac{[\text{CTCl}_3]_2}{[\text{CDCl}_3]_2} = \frac{K_{\text{eq}} F_0}{\alpha} \left[1 - \exp \left(-\alpha k_{-2} \left\{ \frac{V_1}{V_2} \frac{[\text{CDCl}_3]_1}{[\text{CDCl}_3]_2} [\text{OD}]_1 + [\text{OD}]_2 \right\} t \right) \right] \quad (6)$$

Plots of the data taken and of Equation (6) are shown in Appendix A. Values for the equilibrium constant and the rate constant are shown in Table II. It can be seen that the equilibrium constant agrees with the statistical mechanics prediction of 0.5 and that the rate constant is on the same order of magnitude as those reported by Hine, Peek, and Oakes (4).

TABLE II: Equilibrium and Rate Constants for Tritium Exchange Reaction

Run #	T (°C)	[⁻ OD] moles/l	K _{eq}	k ₋₂ (1/mole sec)
4 & 5	25	0.391	0.471	0.114
7	25	0.99	0.468	0.084
6	35	0.391	0.442	0.285
8	46	0.391	0.446	1.239

The equilibrium constant is seen to drop with increasing temperature, which again is in agreement with statistical mechanics predictions (3). The nearly identical values at 35 and 45°C are an indication of how little the equilibrium constant varies at elevated temperatures. The variation of the rate constant at different deuterioxide concentrations is not yet understood.

The activation energy was obtained from the Arrhenius expression:

$$k = Ae^{-E_a/RT} \quad (8)$$

where

A = pre-exponential factor (1/mole sec)

E_a = activation energy (kcal/mole)

k = rate constant (1/mole sec)

R = gas constant (1.987 x 10⁻³ kcal/mole °K)

T = temperature (°K)

Figure 1 shows the line fit by least squares to a plot of $\ln k_{-2}$ vs $1/T$. The resulting slope provides an activation energy of 22.6 kcal/mole. From

$$\Delta H^\ddagger = E_a - RT \quad (9)$$

the activation enthalpy is obtained, and the activation entropy is derived from the pre-exponential factor of the Arrhenius expression:

$$\Delta S^\ddagger = R \ln \frac{N_A h A}{RTe} \quad (10)$$

where

$$e = 2.71828$$

$$h = \text{Planck's constant } (1.58 \times 10^{-37} \text{ kcal sec})$$

$$N_A = \text{Avagadro's number } (6.02 \times 10^{23})$$

$$\Delta S^\ddagger = \text{activation entropy (cal/mole } ^\circ\text{K)}$$

These results are summarized in Table III. They are comparable to the results from Hine, Peek and Oakes shown in Table I.

TABLE III: Heat and Entropy of Activation by Temperature for Tritium Exchange from Heavy Water to Chloroform*

$T(^{\circ}\text{K})$	$\Delta H^\ddagger (\text{kcal/mole})$	$\Delta S^\ddagger (\text{cal/mole } ^\circ\text{K})$
298	22.01	13.33
308	21.99	13.26
319	21.97	13.19

*Based on k_{-2} for $\text{CDCl}_3 + \text{D}_2\text{O} \xrightleftharpoons[k_{-2}]{k_1} \text{CTCl}_3 + \text{D}_2\text{O}$

Figure 1. Rate constant (k_2) vs inverse temperature for tritium transfer from D_2O/DTO to $CDCl_3$ (catalyzed by NaOD). Line is least-squares fit of Arrhenius equation.

Only order of magnitude comparisons should be made between the work performed here and that reported by Hine, Peek and Oakes since a different isotope of hydrogen is being used. The uncertainties in values obtained may be a result of several approximations made in this study. One problem is the lack of direct $\text{CDCl}_3\text{-D}_2\text{O}$ solubility data, a problem which may be attacked in the future by scintillation studies. We suspect some significant differences may exist from the $\text{CHCl}_3\text{-H}_2\text{O}$ system, especially in the presence of NaOD.

The slightly smaller rate constants obtained should be expected since this experiment relates the reaction rate to the bulk-phase concentration of the dissolved reactant instead of the dissolved phase concentration, which is assumed to be the same because of instantaneous mass transfer. In fact, the concentrations are not identical at any given time, and a comparison of the differences in rate constants may lead to determination of mass transfer coefficients between the bulk and dissolved phases.

The determination of the equilibrium constant suffers from the inability to accurately measure the DTO concentration. This problem may be approached by obtaining multiple samples of a single DTO stock solution to be used in all later runs. Also, the experiments may be run on an equal molar basis of D_2O and CDCl_3 instead of an equal volume basis to create a greater percentage concentration change of DTO.

A further consideration is the heat of mixing that occurs upon the addition of NaOD to D_2O at the start of the reaction, which alters the temperature of the reaction for early samples. Additionally, the effect of a finite mixing rate may cause problems for experiments with faster reaction rates, though it was judged to be insignificant for these experiments.

It is unclear how to obtain the forward rate constant k_1 from the rate constant k_{-2} that we have obtained. By symmetry considerations, we would propose that the rate of CDCl_3 and CTCl_3 ionization should be roughly equal and $k_1 = k_{-2}$, whereas the rate of chloroform ion reaction with D_2O or DTO is influenced by the symmetry of the water molecules, and $k_{-1} \neq k_2$. This question is still under study.

CONCLUSIONS

The excellent fit of Equation (6) to the data taken when interfacial transfer of tritium is neglected indicates that the exchange of tritium does occur predominately in the dissolved phases. This result suggests the investigation of agents which will increase the solubility of the D_2O - $CDCl_3$ system. Another possibility is performance of the experiment under pressure to allow liquid-liquid contact at higher temperatures than would be permitted by the $CDCl_3$ boiling point of $60.9^\circ C$ at atmospheric pressure. Gas-liquid contacting should also be investigated. At present, J. Maienschein and R. Barry have planned an extensive schedule of tests to examine these possibilities, to determine equilibrium and rate data at sub-ambient temperatures, and to more accurately determine the quantities discussed in this paper.

The combination of rapidly increasing reaction rates at increasing temperatures combined with moderately decreasing equilibrium constants suggests the use of a temperature-staged exchange unit. If the system was placed in close proximity to the heavy water reactor, the feed water would already be preheated. As the water cooled upon passing through the exchange unit, it would also be approaching a greater equilibrium value and thus a greater exchange of tritium. Rough estimates for the size of a packed tower operating at a heavy-water flowrate of 39 gal/hr and $45^\circ C$ call for a cylinder 12 feet high and 2 feet in diameter, with a liquid hold-up time of 25 minutes.

The experimental technique developed here appears to be flexible enough for all further liquid-liquid experiments. It is recommended that a high priority be given to further modification of the DTO sampling technique to improve the precision of both the equilibrium and rate constants.

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APPENDIX A: Experimental Data and Resulting Rate Equation
for Tritium Exchange from Heavy Water to Deuteriochloroform

Figure A-1. Concentration of CTCI₃ vs time for Runs 4 and 5. [NaOD] = 0.39, 25°C. Line is least-squares fit of Eq. (6), with parameters $K_{EQ} = 0.471$, $k_{-2} = 0.114 \text{ (M s)}^{-1}$

Figure A-2. Concentration of CTCl_3 vs time for Run 6. $[\text{NaOD}] = 0.39$, 35°C . Line is least squares fit of Eq. (6), with parameters $K_{\text{EQ}} = 0.471$, $k_{-2} = 0.285 \text{ (M s)}^{-1}$.

Figure A-3. Concentration of CTCI₃ vs time for Run 7. [NaOD] = 0.99, 25°C. Line is least-squares fit of Eq. (6), with parameters $K_{EQ} = 0.468$, $k_{-2} = 0.084 \text{ (M s)}^{-1}$

Figure A-4. Concentration of $CTCl_3$ vs time for Run 8. $[NaOD] = 0.39$, $46^\circ C$. Line is least-squares fit of Eq. (6), with parameters $K_{ED} = 0.446$, $k_{-2} = 1.239 \text{ (M s)}^{-1}$

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