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# The Reactions of Recoil Tritium Atoms with Water. II. Reactivity Integral- and Moderator-Isotope Effects in $H_2O$-$D_2O$ Binary Mixtures

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The HT and DT yields from the nuclear transformation of $^6$Li(n,$\alpha$)T in $H_2O$–$D_2O$ binary mixtures were studied in the liquid phase. The $(HT/H_2O)/(DT/D_2O)$ ratio was nearly constant at $1.60 \pm 0.08$ over the whole range of mol fractions of $D_2O$ in the presence of $I_2$ as a scavenger. Using the kinetic model with reasonable assumptions, the relative efficiencies for the kinetic moderation of $H_2O$, HDO, and $D_2O$ were determined. The results indicate that the collision of recoil T atoms with HDO, with a large fractional energy loss, must occur as frequently as with $H_2O$.

As is the case with organic compounds,[1–3] the two most important energetic reactions of recoil T atoms with $H_2O$ or $D_2O$ are the hydrogen abstraction and the hydrogen substitution;

$$T + H_2O(D_2O) \longrightarrow HT + OH(DT+OD) \quad (1)$$

$$T + H_2O(D_2O) \longrightarrow HTO + H(DTO+D) \quad (2)$$

The yields of Reactions 1 and 2 are 11 and 68% with $H_2O$ and 10.6 and 68% with $D_2O$ respectively.[4,5] The apparent absence of the isotope effect must result from the fact that the preference of the abstraction of H over D atoms is counterbalanced by the "moderator" isotope effects[6] of $H_2O$ and $D_2O$ on recoil T atoms.

In a previous paper,[5] the "moderator" isotope effect was estimated to be 1.5 by comparing the acetone-*t* yield at zero mol fraction (m.f.) of acetone in the $H_2O$-acetone and $D_2O$–acetone binary systems. This, in turn, gives the "reactivity integral"[6] isotope effect of 1.5.

The present paper will deal with the recoil T reactions in the $H_2O$–$D_2O$ mixture. This system has the advantage that the relative reactivity of recoil T atoms is directly proportional to the observed HT/DT at any given m.f. of $D_2O$; thus, no correction for the "moderator" isotope effect is required.

## Experimental

The experimental procedure has been described in detail in the previous paper.[5] Five-ml portions of various mixtures of $H_2O$ and $D_2O$ containing 0.025 g of $LiNO_3$ were sealed in a 13-ml quartz ampoule with a breakable tip. The neutron irradiation was carried out in the JRR-4 in a flux of $3 \times 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$ for 1 min. The dose rate of $\gamma$-rays at the irradiation port was estimated to be $1 \times 10^8$ $r \cdot h^{-1}$. During the irradiation, samples were cooled by letting cooling water flow through and were maintained at 20—30 °C.

After the irradiation, the gaseous products collected by means of a Toepler pump were divided into two parts. One of them was injected into an alumina column, 6 m long, for the determination of the product yield. The other was subjected to the isotopic separation. A 5-m ferric oxide-$\gamma$-alumina column was used. The $\gamma$-alumina was 40—60 mesh, chemically coated with $Fe_2O_3$. The column was operated at the temperature of liquid $N_2$. The activity measurement was performed using a gas-flow proportional counter.

The activity of the condensates was measured by means of a liquid scintillation counter. One hundred µl of a solution was dissolved in 10 ml of the liquid scintillator, prepared by dissolving 112 g of naphthalene, 275 mg of POPOP, and 6 g of DPO in 1 l of dioxane.

The conversion factor required to correlate the activities measured by the two different methods was obtained in the following experiments. An aliquot of the tritiated water of a known specific activity was passed through a carbon-wool column heated at 1100 °C. The resulting hydrogen was directly introduced into the radio-gas chromatograph. Another aliquot of the water was radio-assayed by means of the liquid scintillation counter. The counting efficiency of the radio-gas chromatograph was 1/3.8 of that of the liquid scintillation counter. The activities of the gaseous products can, then, be compared with those of the liquid phase.

## Results and Discussion

*Relative Reactivities of O–H and O–D Bonds.* In Fig. 1 the HT and DT yields in 0.07 M $LiNO_3$ solution containing $1.2 \times 10^{-3}$ M $I_2$ are plotted as a function of the m.f. of $D_2O$. It seems that $H_2O$ is more efficient than $D_2O$ as a moderator for recoil T atoms, since the HT yield curve is slightly convex upward, while the DT yield curve is concave. However, at a given composition of $H_2O$ and $D_2O$, a comparison of the relative reactivities of O–H and O–D bonds does not require any correction for the "moderator" isotope

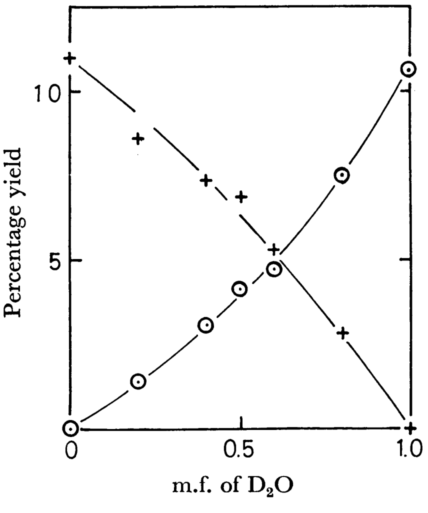

Fig. 1. Yields of HT and DT formed by reactions of recoil T atoms in $H_2O$–$D_2O$ binary mixtures.
⊙: percentage yield of DT, +: percentage yield of HT.

Table 1. Relative reactivities of O–H and O–D bonds, and relative moderating abilities of $H_2O$, HDO, and $D_2O$ in $H_2O$–$D_2O$ binary mixtures

| m.f. of $D_2O$ | $HT/H_2O$ (%/m. f.) | $DT/D_2O$ (%/m. f.) | $\frac{HT/H_2O}{DT/D_2O}$ | $\alpha_{HDO}/\alpha_{H_2O}$ | $\alpha_{HDO}/\alpha_{D_2O}$ |
|---|---|---|---|---|---|
| 1.0 | — | 10.6 | — | — | — |
| 0.8 | 14.0 | 9.38 | 1.49 | 1.01 | 1.35 |
| 0.6 | 13.3 | 7.83 | 1.69 | 0.91 | 1.57 |
| 0.5 | 12.5 | 8.20 | 1.68 | 0.76 | 1.33 |
| 0.4 | 12.3 | 7.75 | 1.59 | 0.90 | 1.40 |
| 0.2 | 10.8 | 7.00 | 1.54 | 1.13 | 1.62 |
| 0.0 | 11.0 | — | — | — | — |
| | | | av. 1.60±0.08 | $\alpha_{H_2O}$: $\alpha_{HDO}$: $\alpha_{D_2O}$ =1.56±0.16: 1.45±0.12: 1 | |

effect, since both bonds are exposed to the same tritium flux. Thus, the $(HT/H_2O)/(DT/D_2O)$ ratio is directly proportional to the reactivity of these bonds. The values summarized in Table 1 are almost constant at 1.60±0.08 over the whole range of the m.f. of $D_2O$. This suggests that the hot reactions with the two bonds have very similar energy dependences and can be used for estimates of the magnitude of the "reactivity integral" isotope effect, $I_{HT}/I_{DT}$.

In the present case, the $(HT/H_2O)/(DT/D_2O)$ ratio is related to $I_{HT}/I_{DT}$ by the following equation;[7]

$$\frac{(HT/H_2O)}{(DT/D_2O)} = \frac{S_{OH}}{S_{OD}} \cdot \frac{I_{HT}}{I_{DT}} \tag{3}$$

where $S_{OH}$ and $S_{OD}$ are the collision cross sections for the T atoms with O–H and O–D bonds, averaged over the proper range of energies.

With the value of 1.60±0.08 for the $(HT/H_2O)/(DT/D_2O)$ ratio, Eq. 3 can be simplified as;

$$\frac{I_{HT}}{I_{DT}} = 1.60 \times \frac{S_{OD}}{S_{OH}} \tag{4}$$

Therefore, if the collision cross sections of these bonds are equal, the "reactivity integral" isotope effect is determined to be 1.60±0.08.

However, in the mixtures of $H_2O$ and $D_2O$ isotopic mixing occurs;

$$H_2O + D_2O \rightleftharpoons 2HDO \tag{5}$$

Its equilibrium constant has been reported to be 3.78±0.03 by Pyper *et al.*[8] and 3.94±0.03 by Gold *et al.*[9] Thus, the actual reaction systems are composed of $H_2O$, HDO, and $D_2O$, and the value of 1.60 must be the overall "reactivity integral" isotope effect between the O–H and O–D bonds in these chemical forms. In the abstraction of hydrogen from $D_2O$, both the primary and the secondary isotope effects exist, while from HDO either the primary or the secondary isotope effect exists, depending upon which hydrogen atom is abstracted. If the secondary isotope effect on the abstraction of hydrogen is as important as in the substitution of hydrogen[1,2] the yield must be larger from $H_2O$ than from HDO on a per-bond basis. The HT/DT ratios from various reaction systems, including the $CH_4$–$CD_4$, $CH_2D_2$, and $CH_3F$–$CD_3F$ systems, always stay within the range of 1.28—1.35.[2] These results are consistent only with the view that the primary isotope effect makes a major contribution to the isotope effect observed. Thus, although no unequivocal data are available, it may be considered that, in the present reaction system, the secondary isotope effect is less important than the primary isotope effect.

*Relative Moderating Abilities of $H_2O$, HDO, and $D_2O$.* The Estrup-Wolfgang kinetic theory[2] incorporates no mechanistic assumptions and has successfully been applied to various reaction systems. However, it has very seldom been applied to the condensed phases,[12] since therein the reactions of recoil atoms are often influenced by the various effects characteristic of the liquid phase, such as the cage effect and the local heating of the matrix.

Data on the reactions of recoil T atoms in condensed phases are, in virtually all cases, completely consistent with the model based on reactions in the gaseous phases. It has been reported that the reactions with various hydrocarbons gave similar yields in the gas and liquid phases.[2] The only differences found could be attributed to the more rapid collisional deactivation of excited products in the liquid phases. This clearly indicates that the effects which usually play a significant role in the liquid phase make only a minor contribution to the reactions of recoil T atoms in the liquid phases. Thus, the application of the kinetic theory to the present reaction systems is reasonable.

According to the kinetic theory, the probability that a hot atom will react with the component, j, to form the product, i, is expressed by this equation;[13]

$$P_i = \left(\frac{N_i}{N_s}\right) = \left(\frac{f_j}{\alpha}\right) I_i - \left(\frac{f_j}{\alpha}\right)^2 K_i + \cdots \tag{6}$$

where $I_i$ and $K_i$ are the "reactivity integral"[14] and the "energy shadowing" terms respectively. The $f_j$ is the collision probability of a hot atom with the component, j. In the present reaction mixtures,

$$\begin{aligned} f_{H_2O} &= (X_{H_2O} \cdot S_{H_2O})/(\textstyle\sum X_j S_j) \\ f_{HDO} &= (X_{HDO} \cdot S_{HDO})/(\textstyle\sum X_j S_j), \text{ and} \\ f_{D_2O} &= (X_{D_2O} \cdot S_{D_2O})/(\textstyle\sum X_j S_j) \end{aligned} \tag{7}$$

where $\sum X_j S_j = X_{H_2O} \cdot S_{H_2O} + X_{HDO} \cdot S_{HDO} + X_{D_2O} \cdot S_{D_2O}$ and where $X_j$ is the m.f. of the component, j. The $\alpha$ is the weighted sum of the average energy loss upon collision with $H_2O$, HDO, and $D_2O$:

$$\alpha = \alpha_{H_2O} \cdot f_{H_2O} + \alpha_{HDO} \cdot f_{HDO} + \alpha_{D_2O} \cdot f_{D_2O} \tag{8}$$

The sum of the HT and DT yields is not large and is almost constant at 11% over the whole range of the m.f. of $D_2O$. Thus, if the energy range of the recoil T atoms needed to produce HT or DT lies entirely above the range to produce HTO or DTO, one can reasonably ignore the "energy shadowing" term. On the other hand, as it is probable that the former lies below the latter, or that both energy ranges overlap each other, one must take into account the "energy shadowing" effects caused by the substitution reactions.

However, as for the reactions among the isotopic water molecules, it is considered unlikely that the shapes and the energy ranges of the excitation curves for the abstraction and substitution of hydrogen vary significantly with the reactant molecules. This consideration leads to the view that a fraction of recoil T atoms, eliminated by the substitution reaction prior to the abstraction reaction, is close to the constant, $K$, among the samples. This is consistent with the fact that the total water-*t* yield is almost constant over the whole range of the m.f. of $D_2O$. Thus, the $(1-K)\cdot N_s$ atoms of tritium are available for abstraction reaction. Consequently, as a reasonable approximation, one can derive the following equations on the assumption that $S_{H_2O}=S_{HDO}=S_{D_2O}$:

i) for the case of a single reactant of $H_2O$ or $D_2O$;

$$\frac{N_{HT}}{(1-K)\cdot N_s}=\frac{f_{H_2O}}{\alpha_{H_2O}}I_{H_2O},\quad \frac{I_{H_2O}\cdot(1-K)}{\alpha_{H_2O}}=0.11 \tag{9}$$

$$\frac{N_{DT}}{(1-K)\cdot N_s}=\frac{f_{D_2O}}{\alpha_{D_2O}}I_{D_2O},\quad \frac{I_{D_2O}\cdot(1-K)}{\alpha_{D_2O}}=0.106 \tag{10}$$

ii) for the case of a binary mixture;

a. the HT yield from the reactions with $H_2O$;

$$\left(\frac{N_{HT}}{N_s}\right)_{H_2O}=(1-K)\cdot\frac{f_{H_2O}}{\alpha}\cdot I_{H_2O}$$
$$=\frac{(1-K)\cdot(X_{H_2O}/\alpha_{H_2O})\cdot I_{H_2O}}{X_{H_2O}+(\alpha_{HDO}/\alpha_{H_2O})\cdot X_{HDO}+(\alpha_{D_2O}/\alpha_{H_2O})\cdot X_{D_2O}} \tag{11}$$

b. the HT yield from the reactions with HDO;

$$\left(\frac{N_{HT}}{N_s}\right)_{HDO}=\frac{(1-K)\cdot(X_{HDO}/\alpha_{H_2O})\cdot I_{HDO}}{X_{H_2O}+(\alpha_{HDO}/\alpha_{H_2O})\cdot X_{HDO}+(\alpha_{D_2O}/\alpha_{H_2O})\cdot X_{D_2O}} \tag{12}$$

By equating $I_{HDO}$ with $(I_{H_2O})/2$ and by substituting Eq. 9 into Eqs. 11 and 12, we obtain the following equation for the total HT yield from the $H_2O$–$D_2O$ binary mixtures:

$$\left(\frac{N_{HT}}{N_s}\right)=\frac{0.11\cdot X_{H_2O}+0.055\cdot X_{HDO}}{X_{H_2O}+(\alpha_{HDO}/\alpha_{H_2O})\cdot X_{HDO}+(\alpha_{D_2O}/\alpha_{H_2O})\cdot X_{D_2O}} \tag{13}$$

The corresponding equation for the total DT yield from the mixture is;

$$\left(\frac{N_{DT}}{N_s}\right)=\frac{0.106\cdot X_{D_2O}+0.053\cdot X_{HDO}}{X_{D_2O}+(\alpha_{HDO}/\alpha_{D_2O})\cdot X_{HDO}+(\alpha_{H_2O}/\alpha_{D_2O})\cdot X_{H_2O}} \tag{14}$$

Thus, if we know the $(\alpha_{H_2O}/\alpha_{D_2O})$ value, the relative efficiency of $H_2O$, HDO, and $D_2O$ as the kinetic moderators can be determined using Eqs. 13 and 14. In Table 1 are also included the values of $(\alpha_{HDO}/\alpha_{H_2O})$ and $(\alpha_{HDO}/\alpha_{D_2O})$. For the calculation, the $\alpha_{H_2O}/\alpha_{D_2O}$ value of 1.5 was used, this value has previously been determined from the ratios of the acetone-*t* yields at zero m.f. of acetone in the $H_2O$–acetone and $D_2O$–acetone systems.[5] As an average, the values of 1.56±0.16 for $\alpha_{H_2O}/\alpha_{D_2O}$ and of 1.45±0.12 for $\alpha_{HDO}/\alpha_{D_2O}$ are deduced. Although the qualitative and quantitative significance of the present relative moderating abilities is largely dependent on the model and the asumptions introduced, the uncertainties involved do not affect the semiquantitative conclusion: $\alpha_{H_2O}\approx\alpha_{HDO}>\alpha_{D_2O}$.

A non-reactive collision of a recoil T atom with a molecule is very "cushioning".[7] In such a collision, a large fraction of the excess kinetic energy of the atom is transferred to the various degrees of freedoms in the struck molecule. The complexity of the molecule and the case of the energy transfer through the bonds are considered to be the important parameters governing the efficiency of the energy transfer. The consequence of the former is well demonstrated by the experimental results[7,15]: the α values increase in this order, $D_2$, $CH_4$, $C_2H_6$, *n*-$C_3H_8$, *n*-$C_4H_{10}$, *n*-$C_5H_{12}$, and *iso*-$C_5H_{12}$, indicating their dependence on the number of atoms involved and the complexity of the molecule. On the other hand, the latter parameter is closely related to the vibrational frequency of the bonds, since the energy transfer occurs through the bond vibrations: as the frequency becomes higher, the transfer becomes faster. The present results are consistent with this consideration: the O–H bond has a vibrational frequency higher than that of the O–D bond,[16] and the collision of recoil T atoms with HDO, with a large fractional energy loss, must occur as frequently as with $H_2O$.

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