Hydrogen Isotope Disproportionation and Fractionation Equilibria in the H₂O–D₂O Solvent System. IV.* Fractionation of Deuterium between 3,3-Dimethyl-2-butanone and Water

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Fractionation of deuterium between 3,3-dimethyl-2-butanone and water has been studied at 298.15 K in different H₂O–D₂O liquid mixtures. A value of 0.840(6) was obtained for the fractionation factor of 3,3-dimethyl-2-butanone and a value of 2.85(6) for the equilibrium constant of the disproportionation reactions of the substrate, assuming the equilibrium constants of the two disproportionation reactions to be equal to each other. The effect of a breakdown of the rule of the geometric mean in the isotope disproportionation reactions of the substrate and the solvent water on the isotope fractionation equilibria of substrates with three exchangeable hydrogens is discussed.

In previous papers,¹⁻³ the deuterium isotope fractionation equilibria of substrates with one and two exchangeable hydrogens were studied in the H₂O–D₂O solvent system. When fractionation factors for substrates containing three exchangeable hydrogens are measured, there are two isotope disproportionation equilibria of the substrate in addition to the isotope disproportionation reaction of solvent water to be taken into account in discussing the fractionation equilibria. To simplify the calculations, the rule of the geometric mean⁴ (RGM) is usually assumed to be valid for the isotope disproportionation equilibria. There is, however, no experimental verification of the applicability of the RGM to the substrates with three exchangeable hydrogens. On the other hand, it has been shown that the RGM does not hold for the isotope disproportionation equilibrium of solvent water¹⁻⁹ and that the neglect of the deviations from the RGM in the isotope disproportionation reaction of solvent water may introduce an error of about 6 % in the fractionation factors.¹⁸ The aim of this work was to obtain more experimental information on the hydrogen isotope disproportionation equilibria in the liquid phase and on the combined effect of the isotope disproportionation in substrate and solvent water on the fractionation equilibria.

** Experimental **

Materials. 3,3-dimethyl-2-butanone (Fluka AG, purum) was distilled once before used.

For the equilibration experiments, the sodium hydroxide–sodium deuterioxide solutions, in which the deuterium isotope mole fraction of water varied between 0.1 and 0.9, were prepared as described in Ref. 3.

The deuterium oxide used was a product of Norsk Hydro-elektrisk Kvaelstofaktieselskab. The deuterium isotope mole fraction of D₂O was reported to be 0.998.

Equilibration experiments. The performance of equilibrations was similar to that described in Ref. 3. The concentration of the catalyst was 0.07 mol dm⁻³, the volume of the catalyst – water solution was 40 cm³, the amount of substrate was 0.0046 mol and the time of equilibration was 3 h.
Table 1. Mole ratios of deuterium and protium in 3,3-dimethyl-2-butaneol equilibrated in different H₂O—D₂O mixtures and the experimental fractionation factors \( q'(\text{SH}_3) \) at 298.15 K.

<table>
<thead>
<tr>
<th>( x(\text{D}:\text{L}:\text{O}) )</th>
<th>( \frac{n(\text{D}:\text{SL}_3)}{n(\text{H}:\text{SL}_3)} )</th>
<th>( q'(\text{SH}_3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.116</td>
<td>0.1105(14)</td>
<td>0.842(11)</td>
</tr>
<tr>
<td>0.213</td>
<td>0.222(2)</td>
<td>0.821(8)</td>
</tr>
<tr>
<td>0.325</td>
<td>0.400(6)</td>
<td>0.832(13)</td>
</tr>
<tr>
<td>0.434</td>
<td>0.639(9)</td>
<td>0.833(11)</td>
</tr>
<tr>
<td>0.509</td>
<td>0.873(8)</td>
<td>0.842(8)</td>
</tr>
<tr>
<td>0.600</td>
<td>1.266(6)</td>
<td>0.844(4)</td>
</tr>
<tr>
<td>0.721</td>
<td>2.181(8)</td>
<td>0.844(3)</td>
</tr>
</tbody>
</table>

\( x(\text{D}:\text{L}:\text{O}) \) is the deuterium isotope mole fraction of water.

Mean values of 4–5 determinations with standard errors of mean.

The experimental fractionation factor is defined by

\[ q'(\text{SH}_3) = \frac{n(\text{D}:\text{SL}_3)/n(\text{H}:\text{SL}_3)}{1 - x(\text{D}:\text{L}:\text{O})} \]

NMR measurements. The measurements were made with a Jeol JNM-PMX 60 NMR spectrometer immediately after the substrate was extracted from the equilibrium mixture. In 3,3-dimethyl-2-butaneol, only the \( \alpha \)-hydrogens are exchangeable under the conditions used in the experiments. Thus the peak due to the protons of the tert-butyl group remains unchanged during deuteriation and acts as an internal standard in the measurements. The positions of the NMR peaks used in the measurements were \( \delta [\text{CH}_3] = 1.09 \text{ ppm} \) and \( \delta (\text{CH}) = 2.05 \text{ ppm} \). 5 to 10 successive integral recordings were carried out from each extract. Before the integrals of the equilibrated substrates, the integrals of undeuterated 3,3-dimethyl-2-butaneol were recorded. The results from the equilibrations are listed in Table 1. In the following text notation \( \text{SH}_3 \) is used for 3,3-dimethyl-2-butaneol \( (\text{CH}_3)_3\text{CCOCH}_3 \).

Discussion

Calculation of \( K(\text{SH}_3 \text{D}) \) and \( K(\text{SHD}_3) \)

When the substrate \( \text{SH}_3 \) containing 3 isotopically exchangeable hydrogens is dissolved in water of arbitrary deuterium content, the following inde-

\[ 0.5 \text{H}_2 \text{O} + 0.5 \text{D}_2 \text{O} = \text{HDO} \]  
\[ 0.5 \text{SH}_3 + 0.5 \text{SD}_3 = \text{SHD}_3 \]  
\[ 0.5 \text{SH}_3 + 0.5 \text{D}_2 \text{O} = 0.5 \text{SD}_3 + 0.5 \text{H}_2 \text{O} \]

In the following approach, it is assumed that in the expressions of equilibrium constants, the activities can be replaced by mole fractions. The equilibrium constants of the equilibria (1), (2), (3) and (4) are expressed by eqns. (5), (6), (7) and (8), respectively.

\[ K(\text{HDO}) = \frac{x(\text{HDO})}{x(\text{H}_2\text{O})^0 \times x(\text{D}_2\text{O})^0} \]  
\[ K(\text{SH}_3 \text{D}) = \frac{x(\text{SH}_3 \text{D})}{x(\text{SH}_3)^0 \times x(\text{SD}_3)^0} \]  
\[ K(\text{SHD}_3) = \frac{x(\text{SHD}_3)}{x(\text{SH}_3)^0 \times x(\text{SD}_3)^0} \]

\[ \varphi(\text{SH}_3) = \left[ \frac{x(\text{SD}_3)}{x(\text{SH}_3)} \right]^0 \times \left[ \frac{x(\text{H}_2\text{O})}{x(\text{D}_2\text{O})} \right]^0 \]

In the equilibrated substrate \( \text{SL}_3 \), the mole ratio of deuterium and protium expressed in terms of the mole fractions of the different \( \text{SL}_3 \) species is given by eqn (9).

\[ \frac{n(\text{D}:\text{SL}_3)}{n(\text{H}:\text{SL}_3)} = \frac{3x(\text{SD}_3) + 2x(\text{SHD}_3) + x(\text{SH}_3 \text{D})}{3x(\text{SH}_3) + 2x(\text{SH}_3 \text{D}) + x(\text{SD}_3)} \]  

Replacing \( x(\text{SH}_3 \text{D}) \) and \( x(\text{SHD}_3) \) in eqn. (9) by the expressions from eqns. (6) and (7) and then using eqn. (8), eqns. (10) can be derived for the computation of the equilibrium constants \( \varphi(\text{SH}_3) \), \( K(\text{SH}_3 \text{D}) \) and \( K(\text{SHD}_3) \) from the experimental data given for 3,3-dimethyl-2-butaneol in Table 1.
\[
3 \left[ \frac{x(D,O)}{x(H,O)} \right]^1 \varphi(SH_3) \] 
\[+ \left[ 2 - \frac{n(D;S;L_2)}{n(H;S;L_2)} \right] K(SHD_2) \frac{x(D,O)}{x(H,O)} \frac{x(D,O)}{x(H,O)} \varphi(SH_3) \]

\[+ \left[ 1 - \frac{n(D;S;L_2)}{n(H;S;L_2)} \right] K(SH,D) \left[ \frac{x(D,O)}{x(H,O)} \right]^1 \varphi(SH_3) - 3 \frac{n(D;S;L_2)}{n(H;S;L_2)} = 0 \]  
(10)

\[
\left[ \frac{x(D,O)}{x(H,O)} \right]^1 = \frac{2x(D;L_2;O)}{4[1 - x(D;L_2;O)]} \]
\[+ \frac{\sqrt{[2x(D;L_2;O) - 1]^2} K(HDO)^2 + 16x(D;L_2;O)}{4[1 - x(D;L_2;O)]} \]
(11)

The ratio \([x(D,O)/x(H,O)]^1\) is a function of the deuterium isotope mole fraction of water, \(x(D;L_2;O)\), and can be calculated from eqn. (11) with different values for \(x(D;L_2;O)\) in Table 1. Eqn. (11) has been derived in the previous paper.¹

The calculations were performed with a DEC system-10 computer. A value of 3.76¹ was used for \(K(HDO)^2\). The computed optimum values are \(\varphi(SH_3) = 0.833(4)\), \(K(SH,D) = 2.77(4)\) and \(K(SHD_2) = 2.94(2)\).

According to the RGM, the equilibrium constants \(K(SH,D)\) and \(K(SHD_2)\) are equal to one another. It seems quite improbable that \(K(SH,D)\) and \(K(SHD_2)\) would differ as much as the values obtained by the method above indicate. Obviously the accuracy of the experimental data is not satisfactory for a determination of \(K(SH,D)\) and \(K(SHD_2)\) separately. Therefore, the values of \(K(SH,D)\) and \(K(SHD_2)\) were also determined assuming that \(K(SH,D) = K(SHD_2)\). This assumption is justified, e.g., on the basis of the theoretical calculations made for the disproportionation reactions of ammonia, \(2 NH_3 + ND_3 = 3 NH_2D\) and \(NH_3 + 2 ND_3 = 3 NHD_2\); the values \(K(NH,D)^1 = 24.61\) and \(K(NHD)^1 = 24.53\) can be calculated from the partition function ratios.¹⁰ These values correspond to a value of 2.91 for both \(K(NH,D)\) and \(K(NHD)\). Likewise, the values of 25.87 and 25.89 have been calculated for the equilibrium constants of the disproportionation reactions of lyonium ions, \(2 H_2O^+ + D,O^+ = 3 H_2DO^+\) and \(H_2O^+ + 2 D,O^+ = 3 HDO^+\), respectively. These values correspond to a value of 2.96 for both \(K(H_2DO^+)\) and \(K(KD,O^+)\).

The fractionation factor \(\varphi'(SH_3)\), which can be determined experimentally, is defined by eqn. (12).

\[
\varphi'(SH_3) = \frac{n(D;S;L_2)}{n(H;S;L_2)} : \frac{n(D;L_2;O)}{n(H;L_2;O)} \]

\[= \frac{3x(SD_3) + 2x(SHD_2) + x(SH,D)}{3x(SH_3) + 2x(SH,D) + x(SH,D)} \]
\[\cdot \frac{2x(H,O) + x(HDO)}{2x(D,O) + x(HDO)}. \]  
(12)

Using eqns. (5), (6), (7) and (8), an expression (13) can be derived for \(\varphi'(SH_3)\). Assuming then that \(K(SH,D) = K(SHD_2) = K(SL_3)\) and solving eqn. (13) for \(K(SL_3)\), eqn. (14) is obtained for the computation of the equilibrium constants \(\varphi(SH_3)\) and \(K(SL_3)\).

With different values of \(\varphi'(SH_3)\) and \([x(D,O)/x(H,O)]^1\) (Table 1 and eqn. (11)), the values \(K(SL_3) = K(SH,D) = K(SHD_2) = 2.85(6)\) and \(\varphi(SH_3) = 0.840(6)\) can be computed for the equilibrium constants of reactions (2), (3) and (4), respectively.
\[
\varphi'(SH_3) = \frac{3 \frac{x(D_2O)}{x(H_2O)} \varphi(SH_3)^2 + 2K(SHD_3) \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi(SH_3) + K(SH_2D)}{3 + 2K(SH_2D) \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi(SH_3) + K(SHD_3) \frac{x(D_2O)}{x(H_2O)} \varphi(SH_3)^2} \cdot \varphi(SH_3). 
\]

\[
2 + \left[ \frac{x(D_2O)}{x(H_2O)} \right] K(HDO) = 3 \cdot \frac{x(D_2O)}{x(H_2O)} + K(HDO) 
\] 

In eqn. (14), the expression for the numerator is

\[
A \left\{ \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi'(SH_3) \right\} = \left\{ 2 + \left[ \frac{x(D_2O)}{x(H_2O)} \right] K(HDO) \right\} \varphi'(SH_3) 
\]

and the expression for the denominator is

\[
B \left\{ \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi'(SH_3) \right\} = \left\{ 2 + \left[ \frac{x(D_2O)}{x(H_2O)} \right] K(HDO) \right\} \left\{ 2 \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi(SH_3) + 1 \right\} 
\]

\[
- \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi'(SH_3) \left\{ 2 + \left[ \frac{x(D_2O)}{x(H_2O)} \right] K(HDO) \right\} \left\{ \left[ \frac{x(D_2O)}{x(H_2O)} \right] \varphi(SH_3) + 2 \right\} . 
\]

**Effect of Values of \( K(SH_2D) \), \( K(SHD_3) \) and \( K(HDO) \) on \( \varphi'(SH_3) \)**

The dependence of the measured fractionation factor \( \varphi'(SH_3) \) on the equilibrium constants \( K(SH_2D) \), \( K(SHD_3) \) and \( K(HDO) \) can be discussed in terms of a relative fractionation factor \( \varphi_r(SH_3) \), for which an expression is here derived.

The limit value for the fractionation factor \( \varphi'(SH_3) \) (v. eqn. 13), when the deuterium content of water approaches zero, is given by eqn. (15). In the previous paper, an expression (16) was given for the relative fractionation factor \( \varphi_r(SH) \) of a substrate with one exchangeable hydrogen. When comparing eqns. (16) and (13), it can be seen that the last factor of eqn. (13) can be replaced by \( 2K(HDO)^{-1} \varphi_r(SH) \).

\[
\lim_{x(D_2O) \to 0} \varphi'(SH_3) = \varphi_r(SH_3) = \frac{3}{2} K(HDO)^{-1} K(SH_2D) \cdot \varphi(SH_3). 
\]

\[
\varphi_r(SH) = \frac{\frac{K(HDO)}{2} \left[ \frac{x(D_2O)}{x(H_2O)} \right]}{K(HDO) + 2 \left[ \frac{x(D_2O)}{x(H_2O)} \right] + K(HDO)} . 
\]
As in the case of the deuterium fractionation between SH₂ and water,¹ an accurate determination of the deuterium – protium ratio in the equilibrated SL₃ by the NMR method is quite difficult at higher solvent deuterium content. With the increasing deuterium content of the substrate, the NMR integral ratio for SL₃ is even more unfavourable than it is for SL₂. In addition, only one model for SH₁ was examined in this work. Therefore, in the following, the dependence of the fractionation factor ϕ₁'(SH₃) on the deuterium content of solvent water is illustrated by giving some different values for K(SH₂D) and K(SH₂D). A value of 3.76 is used for K(HDO).

If the RGM were valid for the isotope disproportionation equilibria (1), (2) and (3), ϕ₁'(SH₃) would be unity over the whole range of x₁(D₃L₂O). Using the value of 0.833 computed for ϕ₁(SH₃) from eqn. (10), the relative fractionation factor ϕ₁(SH₃) was calculated from eqn. (17) with different values for K(SH₂D) and K(SH₂D). The values used in the calculations are: K(SH₂D) = 2.77 and K(SH₂D) = 2.94, which are the values obtained in this work for K(SH₂D) and K(SH₂D) separately from eqn. (10), K(SH₂D) = 2.73 and K(SH₂D) = 2.96, which are the lower and higher error limits of K(SH₂D) and K(SH₂D) respectively, K(SH₂D) = 2.81 and K(SH₂D) = 2.92 which are the higher and lower error limits of K(SH₂D) and K(SH₂D) respectively, obtained in this work. The relative fractionation factor ϕ₁(SH₃) was also calculated assuming that K(SH₂D) = K(SH₂D) = K(SL₃) = 2.85(6) and ϕ₁(SH₃) = 0.840 which are the values computed from eqn. (14). The calculated values of ϕ₁(SH₃) are listed in Table 2.

The maximum value of |1 – ϕ₁(SH₃)| presents the greatest error introduced into the values of ϕ₁(SH₃) by neglecting the deviations from the RGM in the isotope disproportionation equilibria (2) and (3). The error seems to increase the more the values of K(SH₂D) and K(SH₂D) differ from each other. From Table 2, it can also be seen that

<table>
<thead>
<tr>
<th>x(D₃L₂O)⁶</th>
<th>K(SH₂D) = 2.77</th>
<th>K(SH₂D) = 2.94</th>
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<tr>
<td></td>
<td>2.73</td>
<td>2.96</td>
</tr>
<tr>
<td>0.1</td>
<td>1.015</td>
<td>1.022</td>
</tr>
<tr>
<td>0.2</td>
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<td>0.8</td>
<td>1.061</td>
<td>1.079</td>
</tr>
<tr>
<td>0.9</td>
<td>1.053</td>
<td>1.067</td>
</tr>
</tbody>
</table>

*K(HDO) = 3.76. The values of ϕ₁(SH₃) needed in the calculation of ϕ₁(SH₃) are given in the earlier paper.¹
⁶x(D₃L₂O) is the deuterium isotope mole fraction of water.

²²⁵
the deviations from the RGM in the hydrogen isotope disproportionation in $L_2O$ and $SL_2$ cancel each other almost completely when $K(SH_2D) = K(SHD_3) = 2.91$, which is a value involving about the same degree of deviation from the RGM value 3 as the value $3.76^1$ for $K(HDO)$ from the RGM value 2. In such cases, the errors introduced into the values of $\psi(SH_3)$ are negligible.

Fig. 1 illustrates the dependence of the fractionation factor $\psi'(SH_3)$ upon the deuterium isotope mole fraction of water, $x(D/L_2O)$, with different values for equilibrium constants $K(SH_2D)$ and $K(SHD_3)$. At solvent composition of $x(D/L_2O) = 0.5$, the value of $\psi'(SH_3)$ was in each case fixed at 0.837, the mean value of the experimental fractionation factors measured for 3,3-dimethyl-2-butaneone (Table 1). The other values of $\psi'(SH_3)$ for drawing the curves in the above figure were calculated using the $\psi_i(SH_3)$ values given in Table 2. The circles represent the experimental $\psi'(SH_3)$ values from Table 1.

\[ \frac{\text{circles}}{\text{dashed}} = K(SH_2D) = 2.81, \quad K(SHD_3) = 2.92 \]
\[ \frac{\text{broken line}}{\text{dashed}} = K(SH_2D) = 2.77, \quad K(SHD_3) = 2.94 \]
\[ \frac{\text{dotted line}}{\text{dashed}} = K(SH_2D) = 2.73, \quad K(SHD_3) = 2.96. \]

The dependence of $\psi'(SH_3)$ upon $x(D/L_2O)$ would also be the same as that of $\psi'(SH)$ given in the previous paper. From Figs. 1 and 2, it can be seen that the dependence of $\psi'(SH_3)$ upon $x(D/L_2O)$ does not support any great deviations from the RGM. However, since small deviations exist and since the cancellation of the deviations between the isotope disproportionation equilibria of substrate and solvent water may not be complete, it is preferable to carry out the fractionation factor measurements at a solvent composition close to $x(D/L_2O) = 0.5$ rather than at either end of the $x(D/L_2O)$ range to obtain the value of the equilibrium constant $\psi(SH_3)$ of the fractionation reaction (4).

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References


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