

Hydrogen Isotope Disproportionation and Fractionation Equilibria in H₂O–D₂O Solvent System. III.* Fractionation of Deuterium between Methoxymethyl Phenyl Ketone and Water

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Fractionation of deuterium between methoxymethyl phenyl ketone and water has been studied in different H₂O–D₂O liquid mixtures. A value of 1.045(15) was obtained for the fractionation factor of methoxymethyl phenyl ketone and a value of 2.02(5) for the equilibrium constant of the isotope disproportionation reaction of the substrate. The effect of a breakdown of the postulate of the geometric mean in the isotope disproportionation reactions of the substrate and the solvent water on the isotope fractionation equilibria of substrates with two exchangeable hydrogens is discussed.

A breakdown of the postulate of the geometric mean³ (PGM) in the isotope disproportionation equilibria has straightforward consequences for the isotope fractionation equilibria in H₂O–D₂O solvent system. For the deuterium isotope fractionation in substrates with only one exchangeable hydrogen the deviations from the PGM are confined to the solvent water alone. The breakdown of the PGM in the isotope disproportionation equilibrium of the solvent water is reflected in the dependence of the measured fractionation factor on the deuterium content of water.¹ The situation will be more complicated when fractionation factors for substrates containing more than one exchangeable hydrogen are measured. In these cases the disproportionation of hydrogen isotopes in the substrates as well as in the solvent water must be taken into account in discussing the fractionation equilibria. It has been custom-

ary to assume that the PGM holds for the isotope disproportionation equilibria because by means of the PGM the calculations can be appreciably simplified. The possibilities of a detailed experimental study of the applicability of the PGM to isotope disproportionation equilibria have been rather limited. Nearly all the experimental studies carried out are associated with the gas phase.^{4–11} The only liquid phase reaction studied is the disproportionation reaction between H₂O and D₂O.^{1,12–15}

In this work fractionation factor measurements for methoxymethyl phenyl ketone dissolved in water of varying deuterium content were carried out for the purpose of getting more experimental information about the hydrogen isotope disproportionation equilibria in the liquid phase and about the effect of a breakdown of the PGM on the isotope fractionation equilibria of substrates with two exchangeable hydrogens in the H₂O–D₂O solvent system.

EXPERIMENTAL

Materials. Methoxymethyl phenyl ketone was synthesized by a Grignard reaction as described by Moffet and Shriner.¹⁶

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 by weight from pure H₂O and D₂O, adding a suitable amount of NaOL (L=H,D) just before the equilibrations. When calculating the solvent deuterium isotope mole fraction of each solution,

* Parts I and II. See Refs. 1 and 2.

the increase of H₂O or D₂O coming from the added catalyst solution was taken into consideration. The aqueous sodium hydroxide solution was prepared from a standard Titrisol solution (E. Merck AG). The corresponding sodium deuterioxide solution was made by dissolving metallic sodium in deuterium oxide under toluene in a separating funnel. The base concentration of the sodium deuterioxide solution was determined by titration with known acid solution.

The deuterium oxide used in the experiments was a product of *Norsk Hydro-elektrisk Kvaestofaktieselskab*. The deuterium isotope mole fraction of D₂O was reported to be 0.998.

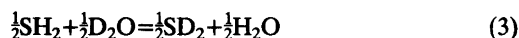
Equilibration experiments. In the equilibrations the substrate-catalyst-water mixtures were shaken in 50 cm³ separating funnels surrounded by a jacket for water circulation. The system was held at a constant temperature of 25 °C within ±0.1 °C with water circulating from a Lauda thermostat. The time of equilibration was maintained about ten times longer than the time that was found necessary just to attain the equilibrium. In the equilibrations the concentration of catalyst was 0.05 mol dm⁻³, the volume of catalyst-water solution was 40 cm³, the amount of substrate was 0.006 mol and the time of equilibration was 3 h. After the equilibrium was reached, 10 cm³ samples were taken from the equilibrium mixtures by means of a semiautomatic pipette. The samples were transferred to 25 cm³ separating funnels containing an acid solution for neutralization of the sample and carbon tetrachloride for extraction of the equilibrated substrate. From each equilibrium mixture six samples were taken. To get the reference spectrum from undeuteriated methoxymethyl phenyl ketone in the conditions corresponding to those of the equilibrations, the CH₃OCH₂COC₆H₅-NaOH-H₂O mixture was also shaken at the same time with CH₃OCH₂COC₆H₅-NaOL-L₂O mixtures (L=H,D). All the mixtures were handled in the same way after equilibration. After the extraction the deuterium content of the equilibrated methoxymethyl phenyl ketone was determined by ¹H NMR measurements.

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 methoxymethyl phenyl ketone only the α-hydrogens are exchangeable under the conditions used in the experiments. Thus the peak due to the protons of the methoxy group remains unchanged during deuteration and acts as an internal standard in the measurements. The positions of the NMR peaks used in the measure-

ments were δ(OCH₃)=3.36 ppm and δ(CH₂)=4.50 ppm. Five to ten successive integral recordings were carried out from each extract. Before the integrals of the equilibrated substrates, the integrals of undeuteriated methoxymethyl phenyl ketone were recorded. The results from the equilibrations are listed in Table 1. In the following text notation SH₂ is used for methoxymethyl phenyl ketone.

DISCUSSION

Calculation of K(SHD). When a substrate SH₂ containing two exchangeable hydrogens is dissolved in water of arbitrary deuterium content, the following independent equilibria, written for one exchangeable hydrogen, are set up: disproportionation equilibrium (1) between isotopically different waters, isotope disproportionation equilibrium (2) of the substrate SL₂ (L=H,D) and isotope fractionation equilibrium (3) between the substrate and the solvent water. Other isotope exchange equilibria involved can be presented by combinations of the equilibria (1)–(3).



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) and (3) are expressed by eqns. (4), (5) and (6).

$$K(\text{HDO}) = \frac{x(\text{HDO})}{x(\text{H}_2\text{O})^{\frac{1}{2}}x(\text{D}_2\text{O})^{\frac{1}{2}}} \quad (4)$$

$$K(\text{SHD}) = \frac{x(\text{SHD})}{x(\text{SH}_2)^{\frac{1}{2}}x(\text{SD}_2)^{\frac{1}{2}}} \quad (5)$$

$$\phi(\text{SH}_2) = \left[\frac{x(\text{SD}_2)}{x(\text{SH}_2)} \right]^{\frac{1}{2}} \left[\frac{x(\text{H}_2\text{O})}{x(\text{D}_2\text{O})} \right]^{\frac{1}{2}} \quad (6)$$

In the equilibrated substrate SL₂ the mole ratio of deuterium and protium expressed in terms of the mole fractions of the different SL₂ species, is given by eqn. (7).

$$\frac{n(\text{D};\text{SL}_2)}{n(\text{H};\text{SL}_2)} = \frac{2x(\text{SD}_2)+x(\text{SHD})}{2x(\text{SH}_2)+x(\text{SHD})} \quad (7)$$

Replacing $x(\text{SHD})$ in eqn. (7) by the expression obtained from eqn. (5) for $x(\text{SHD})$ and then using eqn. (6), a relationship (8) (Scheme 1) is obtained for the computation of the equilibrium

$$2 \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \phi(\text{SH}_2)^2 + \left[1 - \frac{n(\text{D};\text{SL}_2)}{n(\text{H};\text{SL}_2)} \right] \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} K(\text{SHD}) \phi(\text{SH}_2) - 2 \frac{n(\text{D};\text{SL}_2)}{n(\text{H};\text{SL}_2)} = 0 \quad (8)$$

$$\left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} = \frac{[2x(\text{D};\text{L}_2\text{O})-1]K(\text{HDO})}{4[1-x(\text{D};\text{L}_2\text{O})]} + \quad (9)$$

$$\frac{\sqrt{[2x(\text{D};\text{L}_2\text{O})-1]^2 K(\text{HDO})^2 + 16x(\text{D};\text{L}_2\text{O})[1-x(\text{D};\text{L}_2\text{O})]}}{4[1-x(\text{D};\text{L}_2\text{O})]}$$

$$\begin{aligned} \phi'(\text{SH}_2) &= \frac{n(\text{D};\text{SL}_2)}{n(\text{H};\text{SL}_2)} \cdot \frac{n(\text{D};\text{L}_2\text{O})}{n(\text{H};\text{L}_2\text{O})} \\ &= \frac{2x(\text{SD}_2)+x(\text{SHD})}{2x(\text{SH}_2)+x(\text{SHD})} \cdot \frac{2x(\text{H}_2\text{O})+x(\text{HDO})}{2x(\text{D}_2\text{O})+x(\text{HDO})} \end{aligned} \quad (10)$$

$$\phi'(\text{SH}_2) = \phi(\text{SH}_2) \frac{2 \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \phi(\text{SH}_2) + K(\text{SHD})}{2 + \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} K(\text{HDO})} \cdot \frac{2 + \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} K(\text{HDO})}{2 \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \phi(\text{SH}_2) K(\text{SHD}) + \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + K(\text{HDO})} \quad (11)$$

$$\lim_{x(\text{D};\text{L}_2\text{O}) \rightarrow 0} \phi'(\text{SH}_2) = \phi_0(\text{SH}_2) = K(\text{HDO})^{-1} K(\text{SHD}) \phi(\text{SH}_2) \quad (12)$$

$$\phi_r(\text{SH}) = \frac{1}{2} \cdot \frac{K(\text{HDO})^2 x(\text{D}_2\text{O}) + 2x(\text{HDO})}{2x(\text{D}_2\text{O}) + x(\text{HDO})} \quad (13)$$

$$\phi_r(\text{SH}) = \frac{1}{2} K(\text{HDO}) \frac{K(\text{HDO}) \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + 2}{2 \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} + K(\text{HDO})} \quad (14)$$

$$\frac{\phi'(\text{SH}_2)}{\phi_0(\text{SH}_2)} = \phi_r(\text{SH}_2) = \phi_r(\text{SH}) 2K(\text{SHD})^{-1} \frac{2 \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \phi(\text{SH}_2) + K(\text{SHD})}{2 + \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \phi(\text{SH}_2) K(\text{SHD})} \quad (15)$$

Scheme 1.

Table 1. Mole ratios of deuterium and protium in methoxymethyl phenyl ketone equilibrated in different H₂O–D₂O mixtures and the experimental fractionation factors $\phi'(\text{SH}_2)$ at 298.15 K.

$x(\text{D};\text{L}_2\text{O})^a$	$\frac{n(\text{D};\text{SL}_2)^b}{n(\text{H};\text{SL}_2)}$	$\phi'(\text{SH}_2)^{b,c}$
0.108	0.1302(13)	1.075(10)
0.214	0.293(3)	1.077(9)
0.322	0.503(4)	1.058(9)
0.400	0.709(7)	1.063(10)
0.528	1.159(5)	1.036(5)
0.626	1.770(13)	1.057(8)
0.731	2.758(11)	1.015(4)
0.797	4.01(3)	1.020(8)

^a $x(\text{D};\text{L}_2\text{O})$ is the deuterium isotope mole fraction of water. ^b Mean values of six determinations with standard errors of mean. ^c The experimental fractionation factor is defined by $\phi'(\text{SH}_2) = \{n(\text{D};\text{SL}_2)/n(\text{H};\text{SL}_2)\} / \{x(\text{D};\text{L}_2\text{O})/[1-x(\text{D};\text{L}_2\text{O})]\}$.

constants $\phi(\text{SH}_2)$ and $K(\text{SHD})$ from the experimental data given for methoxymethyl phenyl ketone in Table 1. The ratio $[x(\text{D}_2\text{O})/x(\text{H}_2\text{O})]^2$ is a function of the deuterium isotope mole fraction of water, $x(\text{D};\text{L}_2\text{O})$, and can be calculated from eqn. (9) with different values for $x(\text{D};\text{L}_2\text{O})$ in Table 1. Eqn. (9) has been derived in the previous paper.¹ The calculations were performed with a DECsystem 10 computer. A value of 3.76 was used for $K(\text{HDO})^2$.¹ The computed optimum values are $\phi(\text{SH}_2)=1.045(15)$ and $K(\text{SHD})=2.02(5)$. Within the experimental error the value of $K(\text{SHD})$ is the same as the PGM value 2.

Effect of Values of $K(\text{SHD})$ and $K(\text{HDO})$ on $\phi(\text{SH}_2)$. The dependence of the measured fractionation factor $\phi'(\text{SH}_2)$ on the equilibrium constants $K(\text{SHD})$ and $K(\text{HDO})$ can be discussed in terms of a relative fractionation factor $\phi_r(\text{SH}_2)$, for which an expression will be derived. The experimentally determinable fractionation factor $\phi'(\text{SH}_2)$ is defined by eqn. (10). Replacing $x(\text{SHD})$ and $x(\text{HDO})$ in eqn. (10) by expressions from eqns. (5) and (4) and then using eqn. (6), the experimental fractionation factor $\phi'(\text{SH}_2)$ can be presented in the form of eqn. (11). The limit value for the fractionation factor $\phi'(\text{SH}_2)$, when the deuterium content of water closes on zero, is given by eqn. (12).

In the previous paper¹ an expression (13) was given for the relative fractionation factor $\phi_r(\text{SH})$ of a substrate with one exchangeable hydrogen. Eqn. (13) can be presented in the form of eqn.

(14), replacing $x(\text{HDO})$ in eqn. (13) by $K(\text{HDO})x(\text{H}_2\text{O})/x(\text{D}_2\text{O})^2$ [cf. eqn. (4)]. Comparing eqn. (11) with eqn. (14) it is found that the last factor in eqn. (11) can be replaced by the expression $2K(\text{HDO})^{-1}\phi_r(\text{SH})$. Dividing then eqn. (11) by eqn. (12), an expression (15) is obtained for the relative fractionation factor $\phi_r(\text{SH}_2)$.

Taking into account the fact that with the increasing deuterium content of SL_2 an accurate determination of the deuterium–protium ratio in SL_2 by the NMR method becomes more difficult, the values obtained at solvent compositions of a higher deuterium content may not be as reliable as those obtained at solvent compositions of a lower deuterium content. Therefore, it would perhaps not be quite justified to compute any exact value for $K(\text{SHD})$ from eqn. (8). In addition, only one model of SH_2 was examined in this work. Thus in the following the dependence of the fractionation factor $\phi'(\text{SH}_2)$ upon the deuterium isotope mole fraction of water, $x(\text{D};\text{L}_2\text{O})$, is discussed by giving some different values for $K(\text{SHD})$. A value of 3.76^2 is used for $K(\text{HDO})$.¹ If the PGM were to be valid for the isotope disproportionation reactions (1) and (2), the experimental fractionation factor $\phi'(\text{SH}_2)$ would be constant and the value of the relative fractionation factor $\phi_r(\text{SH}_2)$ would be unity over the whole range of $x(\text{D};\text{L}_2\text{O})$. Using the value 1.045 for $\phi(\text{SH}_2)$ the relative fractionation factor $\phi_r(\text{SH}_2)$ was calculated from eqn. (15) with different values for $K(\text{SHD})$. The values used in the calculations are: $K(\text{SHD})=2.02$, which is the value computed for $K(\text{SHD})$ in this work, $K(\text{SHD})=1.97$ and 2.07 , which are the error limits of $K(\text{SHD})$ obtained in this work, $K(\text{SHD})=1.94$, which for equilibrium (2) corresponds to the same deviation from the PGM as 3.76^2 for the disproportionation of hydrogen isotopes in water. Calculations were carried out also with the PGM value 2 and with two values of $K(\text{SHD})$ which are appreciably lower than the PGM value. The calculated values of $\phi_r(\text{SH}_2)$ are listed in Table 2.

The maximum value of $|1-\phi_r(\text{SH}_2)|$ presents the greatest error introduced into the values of $\phi(\text{SH}_2)$ by neglecting the deviations from the PGM in the disproportionation equilibrium (2). If the deviation from the PGM for the disproportionation of SHD is the same as for the disproportionation of HDO, the value of $|1-\phi_r(\text{SH}_2)|$ is practically zero over the whole range of $x(\text{D};\text{L}_2\text{O})$ and the cancellation of the deviations from the PGM between the disproportionation equilibria (1) and (2) is complete. In this case the measured fractionation factor is constant and independent of $x(\text{D};\text{L}_2\text{O})$, representing the real

Table 2. Relative fractionation factor $\phi_r(\text{SH}_2)$ calculated with different values for equilibrium constant $K(\text{SHD})$.^a

$x(\text{D};\text{L}_2\text{O})^b$	$K(\text{SHD})$						
	1.80	1.90	1.94	$\phi_r(\text{SH}_2)$ 1.97	2.00	2.02	2.07
0.1	1.016	1.005	1.000	0.997	0.994	0.992	0.986
0.2	1.032	1.009	1.000	0.994	0.988	0.983	0.973
0.3	1.048	1.013	1.000	0.991	0.982	0.975	0.961
0.4	1.064	1.018	1.001	0.988	0.976	0.967	0.948
0.5	1.080	1.022	1.001	0.985	0.970	0.960	0.936
0.6	1.096	1.026	1.001	0.982	0.964	0.952	0.924
0.7	1.112	1.030	1.000	0.978	0.958	0.944	0.912
0.8	1.128	1.034	1.000	0.975	0.952	0.937	0.901
0.9	1.144	1.038	1.000	0.972	0.946	0.929	0.889

^a $K(\text{HDO})=3.76^{1/2}$. The values of $\phi_r(\text{SH})$ needed in the calculation of $\phi_r(\text{SH}_2)$ are given in the previous paper.¹ ^b $x(\text{D};\text{L}_2\text{O})$ is the deuterium isotope mole fraction of water.

equilibrium constant $\phi(\text{SH}_2)$ of the fractionation equilibrium (3). If the PGM is valid for the disproportionation of SHD, *i.e.* if $K(\text{SHD})=2$, the deviations from the PGM are confined to the solvent water. In this case $\phi_r(\text{SH}_2)=\phi_r(\text{SH})$, and the dependence of $\phi_r(\text{SH}_2)$ upon $x(\text{D};\text{L}_2\text{O})$ is the same as for fractionation of a single hydrogen site, the greatest error being about 6%. The correction of $\phi_r(\text{SH}_2)$ to obtain $\phi(\text{SH}_2)$ is in this case the same as that of $\phi_r(\text{SH})$, given in the previous paper.¹

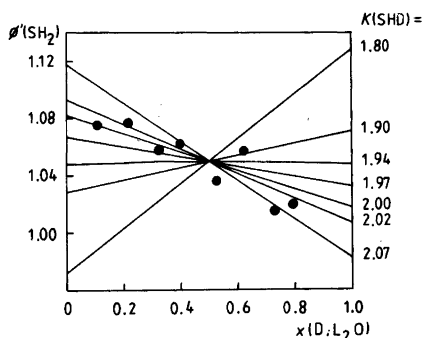


Fig. 1. Dependence of fractionation factor $\phi_r(\text{SH}_2)$ upon the deuterium isotope mole fraction of water, $x(\text{D};\text{L}_2\text{O})$, with different values for equilibrium constant $K(\text{SHD})$. At solvent composition of $x(\text{D};\text{L}_2\text{O})=0.5$ the value of $\phi_r(\text{SH}_2)$ was in each case fixed at 1.050, the mean value of the experimental fractionation factors measured for methoxymethyl phenyl ketone (Table 1.) The other values of $\phi_r(\text{SH}_2)$ for drawing the straight lines were calculated using the $\phi_r(\text{SH}_2)$ values given in Table (2). The circles represent the experimental $\phi_r(\text{SH}_2)$ values from Table (1).

The values in Table 2, which present the dependence of $\phi_r(\text{SH}_2)$ upon $x(\text{D};\text{L}_2\text{O})$ with different values for $K(\text{SHD})$, were calculated using the value 1.045 for $\phi_r(\text{SH}_2)$ in eqn. (15). When different values for $\phi_r(\text{SH}_2)$ were used [$0.5 < \phi_r(\text{SH}_2) < 1.2$] it was found that the value of the fractionation factor itself does not have much effect on the dependence of the relative fractionation factor $\phi_r(\text{SH}_2)$ upon the deuterium content of water.

The dependence of the fractionation factor $\phi_r(\text{SH}_2)$ upon the deuterium isotope mole fraction of water with different values for $K(\text{SHD})$ is illustrated in Fig. 1. Taking into account the uncertainty of the experimental $\phi_r(\text{SH}_2)$ values at higher deuterium contents of solvent water, there seems to be an apparent trend in the experimental values of $\phi_r(\text{SH}_2)$ in the direction required by a value of $K(\text{SHD}) \approx 2$. In any case the trend in the experimental $\phi_r(\text{SH}_2)$ values does not support a value of $K(\text{SHD})$ lower than 1.94.

Since it is apparent that small deviations from the PGM exist also in the disproportionation reactions of substrates with two exchangeable hydrogens and that the cancellation of the deviations between the disproportionation equilibria of substrate and solvent water may not be complete, it is better to carry out the fractionation factor measurements at a solvent composition close to $x(\text{D};\text{L}_2\text{O})=0.5$ rather than at either ends of the $x(\text{D};\text{L}_2\text{O})$ range to obtain the value of the equilibrium constant $\phi(\text{SH}_2)$ of the fractionation reaction (3).

Acknowledgements. Financial aid from the Emil Aaltonen Foundation, and from the Finnish Cultural Foundation is gratefully acknowledged.

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Received January 19, 1984.