

Hydrogen Isotope Disproportionation and Fractionation Equilibria in H₂O/D₂O/Solvent System. V*: Fractionation of Deuterium between Methyl Phenyl Ketone and Water

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Scharlin, P., 1986. Hydrogen Isotope Disproportionation and Fractionation Equilibria in H₂O/D₂O/Solvent System. V. Fractionation of Deuterium between Methyl Phenyl Ketone and Water. – Acta Chem. Scand. A 40: 441–444.

Fractionation of deuterium between methyl phenyl ketone and water has been studied at 298.15 K in different H₂O/D₂O liquid mixtures. A value of 0.908(5) was obtained for the fractionation factor of methyl phenyl ketone. On the basis of the slight dependence of the experimental fractionation factor on the deuterium isotope mole fraction of water, it has been confirmed that there exist small deviations from the rule of the geometric mean in the isotope disproportionation equilibria of substrates containing three exchangeable hydrogens. A value of 2.92(3) has been calculated for the isotope disproportionation equilibria of methyl phenyl ketone assuming the equilibrium constants of the two disproportionation reactions to be equal.

It is customary to assume that the rule of the geometric mean (RGM) is applicable to isotope disproportionation equilibria. According to the RGM, there exist no secondary isotope effects in the disproportionation reactions and equilibria of this type are determined by symmetry considerations alone. Thus, by means of the RGM, the calculations can be appreciably simplified. The possibilities of a detailed experimental study of the applicability of the RGM to isotope disproportionation equilibria are rather limited. Most of the experimental studies are associated with the gas phase.^{5–12} The isotope disproportionation reactions in liquid phase, and especially in a H₂O/D₂O/solvent system are, however, important because a breakdown of the RGM in these reactions and in the corresponding reaction of solvent water has straightforward consequences for isotope fractionation equilibria. Thus far, the only liquid phase reactions studied are the disproportionation of hydrogen isotopes in water,^{1,13–16} the disproportionation of hydrogen in methoxymethyl phenyl ketone,³ (a model for a

substrate containing two exchangeable hydrogens, SH₂), the disproportionation of hydrogen in 3,3-dimethyl-2-butanone,⁴ (a model for a substrate with three exchangeable hydrogens, SH₃) and, quite recently, the disproportionation of hydrogen isotopes in hydrogen sulfide.¹⁷

The disproportionation reactions of substrates of the SH₃ type are of special interest because they are formally similar to the isotope disproportionation reactions of lyonium ions, L₃O⁺ (L = H,D), which are most essential when protolytic reactions in the H₂O/D₂O/solvent system are examined. Since the only means of approaching experimentally the disproportionation reactions of lyonium ions is through suitable model compounds, all information, as reliable as possible, regarding the reactions of substrates with three exchangeable hydrogens in a H₂O/D₂O/solvent system is important. In a previous paper,⁴ the conclusions concerning disproportionation and fractionation reactions of substrates of the SH₃ type were made on the basis of measurements with only one model compound. In the next part of this series it is intended to deal with the disproportionation reactions of lyonium ions,

*Parts I–IV, see Refs. 1–4.

and, therefore, measurements with another model compound were made to get additional information about the isotope exchange reactions of substrates with three exchangeable hydrogens in a H₂O/D₂O/solvent system.

Experimental

Materials. Methyl phenyl ketone from Fluka AG (*puriss p.a.*) was used without further purification. 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 Ega Chemie. The deuterium isotope mole fraction of D₂O was reported to be 0.988.

Equilibration experiments. The performance of equilibrations was similar to that described in Ref. 3. The concentration of catalyst was 0.5 mol dm⁻³, the volume of catalyst/water solution 40 cm³, the amount of substrate 1.6 · 10⁻³ mol and the time of equilibration 9 h.

NMR measurements. The measurements were made with a Jeol GX-400 spectrometer. Under the conditions used in the experiments, only the hydrogens of the methyl group were exchangeable in methyl phenyl ketone. Thus, the peaks due to the protons of the phenyl group remained unchanged during deuteration acting as internal standard in the measurements. The positions of the NMR peaks used in the measurements were δ(CH₃) = 2.43 ppm and δ(C₆H₅) = 7.15–7.50 and 7.80 ppm. The integral from undeuteriated methyl phenyl ketone was recorded before the integrals of the equilibrated substrates. The results from the equilibrations are listed in Table 1. In the following text notation, SH₃ is used for methyl phenyl ketone, C₆H₅COCH₃.

Discussion

Deviations from the RGM in the equilibrium constants of the isotope disproportionation equilibria (1), (2) and (3) are reflected in the equilibrium constant of the isotope fractionation equilibrium (4). For substrate SH₃, the experimental fractionation factor φ'(SH₃) is defined by eqn. (5). If deviations from the RGM exist, they will

Table 1. Mole ratios of deuterium and protium in methyl phenyl ketone equilibrated in different H₂O/D₂O mixtures and the experimental fractionation factors φ'(SH₃) at 298.15 K.

x(D;L ₂ O) ^a	$\frac{n(\text{D};\text{SL}_3)^b}{n(\text{H};\text{SL}_3)}$	φ'(SH ₃) ^{b,c}
0.101	0.1019(46)	0.907(41)
0.143	0.1544(7)	0.925(2)
0.202	0.2356(14)	0.931(6)
0.302	0.392(2)	0.907(5)
0.400	0.607(5)	0.910(8)
0.422	0.658(11)	0.910(15)
0.502	0.936(2)	0.928(2)
0.606	1.387(6)	0.902(4)
0.694	2.102(9)	0.927(4)
0.715	2.278(19)	0.908(8)
0.803	3.685(25)	0.904(6)
0.901	7.91(9)	0.870(10)

^a x(D;L₂O) is the deuterium isotope mole fraction of water.

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

^c The experimental fractionation factor is defined by φ'(SH₃) = {(D;SL₃)/n(H;SL₃)} : {x(D;L₂O)/[1 - x(D;L₂O)]}.



$$\begin{aligned} \varphi'(\text{SH}_3) &= \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} : \frac{n(\text{D};\text{L}_2\text{O})}{n(\text{H};\text{L}_2\text{O})} \\ &= \frac{3x(\text{SD}_3) + 2x(\text{SHD}_2) + x(\text{SH}_2\text{D})}{3x(\text{SH}_3) + 2x(\text{SH}_2\text{D}) + x(\text{SHD}_2)} \\ &\quad \cdot \frac{2x(\text{H}_2\text{O}) + x(\text{HDO})}{2x(\text{D}_2\text{O}) + x(\text{HDO})} \quad (5) \end{aligned}$$

be revealed in the dependence of the experimental fractionation factor of the substrate on the deuterium content of solvent water,^{1,14,15} except in the case where the deviations in the disproportionation equilibrium of water and the corresponding equilibria of substrates are of the same magnitude.^{3,4} Similar deviations will cancel

$$3 \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{3}{2}} \varphi(\text{SH}_3)^3 + \left[2 - \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} \right] K(\text{SHD}_2) \frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \varphi(\text{SH}_3)^2 + \left[1 - 2 \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} \right] K(\text{SH}_2\text{D}) \left[\frac{x(\text{D}_2\text{O})}{x(\text{H}_2\text{O})} \right]^{\frac{1}{2}} \varphi(\text{SH}_3) - 3 \frac{n(\text{D};\text{SL}_3)}{n(\text{H};\text{SL}_3)} = 0 \quad (6)$$

each other almost completely and the experimental fractionation factor would be independent of the deuterium content of solvent water. Likewise, if the RGM were to be valid for the isotope disproportionation equilibria (1), (2) and (3), that is, if $K(\text{HDO}) = 2$ and $K(\text{SH}_2\text{D}) = K(\text{SHD}_2) = 3$, $\varphi'(\text{SH}_3)$ would be constant over the whole range of the deuterium isotope mole fraction of water, $x(\text{D};\text{L}_2\text{O})$. The experimental fractionation factor would then represent the equilibrium constant $\varphi(\text{SH}_3)$ of the fractionation equilibrium (4), as can easily be seen by replacing the mole fractions of species SD_2H , SDH_2 and HDO in eqn. (5) by the expressions obtained from the equations for the equilibrium constants of reactions (1), (2) and (3).

The values of the experimental fractionation factor of methyl phenyl ketone, listed in Table 1, show only a slight dependence on the deuterium content of water. Actually, this variation is so small that the $\varphi'(\text{SH}_3)$ values may be considered to be the same within the limits of experimental error. Taking into account the fact that the RGM is not valid for reaction (1), the nearly uniform values of $\varphi'(\text{SH}_3)$ must indicate small deviations from the RGM in the disproportionation equilibria (2) and (3). On the basis of the discussion in Refs. 3 and 4, these deviations are likely to be of about the same magnitude as in reaction (1). For the calculation of equilibrium constants $K(\text{SH}_2\text{D})$, $K(\text{SHD}_2)$ and $\varphi(\text{SH}_3)$ of reactions (2), (3) and (4), respectively, eqn. (6) was derived.⁴ When deriving eqn. (6), the equilibrium constants $K(\text{SH}_2\text{D})$ and $K(\text{SHD}_2)$ were assumed to be equal to each other. The values obtained from the experimental data given in Table 1 are $K(\text{SL}_3) = 2.92(3)$ for the isotope disproportionation equilibria (2) and (3) and $\varphi(\text{SH}_3) = 0.908(5)$ for the fractionation equilibrium (4). The mole fractions of D₂O and H₂O in different water mixtures were calculated using a value of 3.76¹ for $K(\text{HDO})$.¹

The value of $K(\text{SL}_3) = 2.92(3)$ is in fairly good agreement with the value of 2.85(6) which was obtained in the previous work⁴ for the equilibrium constant of the isotope disproportionation reactions of substrates of type SH_3 . In the present work, a more accurate NMR spectrometer was available for analysing the samples from equilibrated substrate and it was possible to extend the measurements over a wider range of $x(\text{D};\text{L}_2\text{O})$. On this basis, it might be justified to consider the value of $K(\text{SL}_3) = 2.92$ more reliable than the value of 2.85.

The results obtained in this work confirm the conclusions made in the previous work.⁴ Thus, small deviations from the RGM certainly exist but, in many cases, they will probably be of minor significance. As far as the fractionation equilibria are concerned, the fractionation factor measurements at either end of the $x(\text{D};\text{L}_2\text{O})$ range should, however, be avoided to obtain a correct value for the equilibrium constant.

Acknowledgement. I am grateful to Mr. Jorma Mattinen for operating the Jeol GX-400 spectrometer.

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Received February 17, 1986.