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Abstract

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Equilibrium Distribution Coefficients of Deuterium in Isotopic Exchange Between Water and Certain Thiols

Most studies on reactions of hydrogen-isotope exchange have dealt with exchange reactions between water and the groups O—H, N—H, C—H. Studies in the field of hydrogen-isotope exchange reactions between water and the S—H group are few in number ([1–4]).

The equilibrium of the isotopic exchange reaction

$$\mathrm{RSD} + \mathrm{H_2O} \rightleftarrows \mathrm{RSH} + \mathrm{HDO}$$

is customarily characterized by the equilibrium distribution coefficient of deuterium α. The equilibrium distribution coefficient is defined as the ratio of the ratios of the equilibrium concentrations of deuterium and protium in water and in the thiol

$$\alpha = \{[\mathrm{D}]/[\mathrm{H}]\}_{\mathrm{water}}/\{[\mathrm{D}]/[\mathrm{H}]\}_{\mathrm{thiol}} \tag{1}$$

Smoll ([1]) determined the value of α for exchange between water and hydrogen sulfide (2.28 at 15°). For the same exchange reaction Benedict ([2]) gives data of German investigators on the temperature dependence of the equilibrium distribution coefficient of deuterium (2.34 at 25° and 1.92 at 100°). Oden et al. ([3]) obtained a value of α for the exchange reaction between water and ethanethiol (2.32 at 25°). Hutchison and Gill ([4]) give data on the temperature dependence of the equilibrium distribution coefficient for the exchange reaction between water and isopropanethiol (2.02 at 27° and 1.77 at 95°).

The value of α can be calculated when sufficiently detailed spectral data are available. Oden et al. ([3]) calculated the value of α for the exchange reaction between water and ethanethiol and obtained satisfactory agreement with experiment. Since detailed spectral data for thiols of high molecular composition are lacking, the value of α can be estimated only approximately (with an accuracy of ±15%) from the values of the β-factors of the exchanging hydrides, as proposed by Warshel and Waageberg (^{5}). It was of interest to determine experimentally the values of the equilibrium distribution coefficients of deuterium in isotopic exchange reactions between water and certain thiols.

In this work the equilibrium of deuterium-exchange reactions between water and normal butanethiol n-C_4H_9SH, secondary butanethiol sec-C_4H_9SH, isoamylthiol i-$C_5H_{11}SH$, normal hexanethiol n-$C_6H_{13}SH$, and thiophenol C_6H_5SH was investigated. The first four thiols were synthesized from the corresponding alcohols by the method of Frank and Smith (^{6}), and thiophenol from benzenesulfochloride hydride (^{7}). The thiols obtained were thoroughly purified of impurities by distillation on a rectification column packed with glass spirals and having an efficiency of 10–12 plates. The purity of the thiols obtained after distillation was checked by comparing the boiling points and refractive indices with literature data.

The equilibrium distribution coefficients of deuterium α for exchange reactions between water and thiols were determined as follows. Into the apparatus

For the study of equilibrium, 0.5–1 cm^3 of water with a deuterium concentration of ~3 mol.% and 8–15 cm^3 of thiol with the natural deuterium concentration (0.016 mol.%) were introduced. (The apparatus was a glass cylinder 27 mm in diameter, with a capacity of about 40 cm^3, with a side arm 7 mm in diameter and with a constriction in the middle.) The amounts of thiol and water introduced were determined by successive weighing of the equilibrium apparatus on an analytical balance. The side arm was sealed at the constriction, and the equilibrium apparatus was placed in a thermostat, the temperature of which was maintained with an accuracy of \$±\$0.1°. The contents of the equilibrium apparatus were shaken by means of a shaking device at a frequency of 136 oscillations per minute.

Preliminary experiments established that isotopic equilibrium in the exchange reaction between water and thiols is reached in 8–10 h at 20° (in 2 h for exchange with thiophenol) and in 2–4 h at 80°. Therefore, in all experiments on the study of equilibrium, shaking was continued for 12–15 h (5–7 h for exchange with thiophenol) at 20° and for 6–8 h at 80°. After shaking was stopped, the equilibrium apparatus was removed from the thermostat, quickly and carefully wiped with filter paper, the tip of the side arm was broken off, and the contents of the apparatus were transferred to a separatory funnel, through the jacket of which water from the thermostat was circulating. The temperature in the separatory funnel was therefore close to the temperature of the experiment. This made it possible to avoid a shift of the isotopic equilibrium during separation of the layers, since both the experiment itself and the operation of separating the components were carried out at one and the same temperature. The water layer was separated from the thiol by settling and was then purified before isotopic analysis. The purification consisted in passing water vapor over heated copper oxide and in double microdistillation under vacuum (^{8}). The isotopic composition of the water was determined by the drop method. The deuterium concentration in the thiol was not determined; it was calculated from the material balance of deuterium in the system.

In addition to experiments on direct exchange (between deuterium-enriched water and thiol with the natural deuterium concentration), one experiment on reverse exchange at 20° was carried out for each thiol. The method of carrying out the experiments was analogous to that described. For these experiments, water with the natural deuterium concentration and thiols enriched in the preceding direct-exchange experiments to ~1% were used. The reverse-exchange experiments confirmed the attainment of true thermodynamic equilibrium.

The coefficient of equilibrium distribution of deuterium, α, was calculated as follows. If X_0 is the initial deuterium concentration in water, X_p is the deuterium concentration in water after attainment of equilibrium, y_0 is the initial deuterium concentration in the thiol (all concentrations in mol.%), n_t is the number of moles of thiol, and n_v is the number of moles of water, then, on the basis of the definition of α from (1) and the material balance of deuterium in the system, the value of α is determined by the expression

$$\alpha = \frac{X_p}{100 - X_p} \cdot \frac{100 - \left[y_0 + 2\frac{n_t}{n_v}(X_0 - X_p)\right]}{y_0 + 2\frac{n_t}{n_v}(X_0 - X_p)}. \tag{2}$$

Experiments to determine α were carried out in the temperature range 20-80°. For exchange between water and sec-butyl mercaptan, the experiments were carried out in the range 20-70°. For each system, 9-13 experiments were performed, with 2-5 experiments to determine α at each temperature value. The experimental results obtained for determining the coefficient of equilibrium distribution α at different temperatures are given in Table 1. The values of the arithmetic mean errors in the determination of α are also given there.

Table 1

Values of the equilibrium distribution coefficients of deuterium at various temperatures (in parentheses—the number of experiments)

System	20°	40°	50°	60°	80°
Water—*n*-butylthiol	2.20 ± 0.01(4)	2.07 ± 0.07(2)	–	2.02 ± 0.02(2)	1.96 ± 0.02(4)
Water—sec. butylthiol	2.46 ± 0.03(4)	–	2.32 ± 00.0*(2)	–	2.18 ± 0.02**(3)
Water—*u*-amylthiol	2.14 ± 0.03(5)	2.07 ± 0.02(2)	–	1.97 ± 0.01(2)	1.89 ± 0.01(4)

System	20°	40°	50°	60°	80°
Water—*n*-hexylthiol	2.37 ± 0.02(4)	–	2.26 ± 0.03(2)	–	2.16 ± 0.03(4)
Water—thiophenol	2.15 ± 0.02(4)	–	1.95 ± 0.02(2)	–	1.80 ± 0.05(3)

* At 45°
** At 70°

Analysis of equation (2) shows that the accuracy of the determination of α is affected most of all by errors in the determination of X_0 and X_p. Using the drop method of isotope analysis, whose accuracy is ±1% of the measured quantity, it is possible, for the deuterium concentrations used, to obtain values of α with an accuracy, in the worst case, of not less than ±5-6%. As is seen from the values of the arithmetic-mean errors given in Table 1, the error in the determination of α in most cases was ±1%, and only in one case ±3%.

Under the described conditions for carrying out isotope exchange, only the hydrogen isotopes in the S—H group participate in the reaction. The hydrogen isotopes in the C—H groups of the radical residue practically do not participate in the exchange reaction with water ([9]).

The temperature dependence of the equilibrium distribution coefficients of deuterium between water and the thiols studied is presented in Fig. 1 in coordinates $\lg \alpha – 1/T$. The dependences obtained analytically within the temperature range 20-80° can be expressed by the formulas:

Fig. 1. Dependence of the logarithm of the equilibrium distribution coefficient of deuterium α on the reciprocal temperature. *a*—exchange between water and *n*-butylthiol, *b*—exchange between water and sec. butylthiol, *c*—exchange between water and *u*-amylthiol, *d*—exchange between water and *n*-hexylthiol, *e*—exchange between water and thiophenol.

for the exchange reaction between water and normal butylthiol

$$\lg \alpha = 92.07/T + 0.0282 \tag{3}$$

for the exchange reaction between water and secondary butylthiol

$$\lg \alpha = 105.62/T + 0.0313 \tag{4}$$

for the exchange reaction between water and isoamylthiol

$$\lg \alpha = 88.52/T + 0.0283 \tag{5}$$

for the exchange reaction between water and normal hexylthiol

$$\lg \alpha = 69.48/T + 0.1376 \tag{6}$$

for the exchange reaction between water and thiophenol

$$\lg \alpha = 132.93/T - 0.1213 \tag{7}$$

Using the relation proposed by Brodskii (10) between the equilibrium distribution coefficient of deuterium a and the equilibrium constant of the exchange reaction K, one can calculate the heat of the isotope-exchange reactions between water and thiols, ΔH, by the Clapeyron–Clausius formula. The values thus calculated, $-\Delta H$, amount to 600-1200 cal/mole.

The data obtained by us, as well as other data on the equilibrium distribution coefficients of deuterium in isotope-exchange reactions between water and thiols, do not make it possible to establish a direct relation between the magnitude of a and the composition and structure of the radical residue. It is only evident that the influence of the structure and composition of the radical residue on the value of a is small.

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Note: Figure translations are in progress. See original paper for figures.