TRITIUM ISOTOPE FRACTIONATION BETWEEN AMMONIA, METHYLAMINE, DIMETHYLAMINE AND n-BUTANE THIOL

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Isotope exchange between ammonia, methylamine and dimethylamine on the one hand and n-butane thiol on the other has been studied and the tritium isotope fractionation factors have been determined over the temperature range 250–320 K. Theoretical values of the equilibrium isotope effects in these reactions are found to be in good agreement with the experimental results. There exist considerable differences between the values of the fractionation factors for the systems studied showing that the isotope effect depends on the substituent on the amino group.

Introduction

Recently we have published two papers dealing with the tritium isotope fractionation between hydrogen sulfide and methanethiol and between hydrogen sulfide and methanol. Continuing these studies we have determined the tritium isotope fractionation factor between gaseous ammonia, methylamine, dimethylamine and liquid thiol. Instead of methanethiol, previously used in our experiments, we have now selected n-butanethiol to ensure good separation of the reagents (the differences between the partial pressures of these reagents are sufficiently large).

The study of the hydrogen isotope exchange in compounds with NH and SH groups is of interest both from the physicochemical and from the biochemical points of view. Among other aspects it is possible to determine the changes in the physicochemical properties due to hydrogen isotope substitution and to establish the trends enlarging the accumulation of heavy isotopes of hydrogen in a molecule. On the other hand the knowledge of hydrogen isotope fractionation factors between amines and thiols can be of interest for developing technological processes of hydrogen isotope enrichment and/or separation.
Experimental

Tritium radioactive methylamine and dimethylamine were synthesized in the isotope exchange reaction with THO and dried successively over CaCl₂ and CaSO₄ and distilled under high vacuum. The radioactive n-buthanethiol was synthesized in the same way and was dried over 4A molecular sieves and distilled under high vacuum. Untritiated reagents (all from Fluka) were dried and distilled.

Exactly determined amounts of n-C₄H₉SH (1–5 mmol) were introduced into the reaction vessel and the latter was evacuated and placed into the thermostated bath. After the thermal equilibrium had been reached the reaction vessel was filled with gaseous amine. The pressures of NH₃, CH₃NH₂ or (CH₃)₂NH were always lower then the pressures of their saturated vapors at the given temperature. The isotope equilibrium between gaseous amine and liquid thiol was established after 30–60 seconds in the temperature range studied. No measurable changes in the chemical form or in the composition were observed over this short period of reaction. However a small absorption of amine in liquid thiol was observed after a longer time (0.5 hour at 273K).

The radioactivity of amines and thiol was measured in internal gas G–M counter. The details of this procedure were described earlier.²,³ However some corrections had to be made due to the traces of thiol in the portions of amine introduced into the counter. The appropriate corrections for the resolving time of the counter² were taken into account, too.

The tritium isotope fractionation factor, αᵣ, in the reactions:

\[
\begin{align*}
(\text{CH₃})₂\text{NH}^* (v) + \text{RSH} (l) &= (\text{CH₃})₂\text{NH} (v) + \text{RSH}^* (l), \quad (1) \\
\text{CH₃NH}^+_2 (v) + \text{RSH} (l) &= \text{CH₃NH₂} (v) + \text{RSH}^* (l), \quad (2) \\
\text{NH₃} (v) + \text{RSH}^* (l) &= \text{NH₃}^+ (v) + \text{RSH} (l), \quad (3)
\end{align*}
\]

\[\text{R} = \text{n-C₄H₉}\]

was calculated from the relation:

\[
\alphaᵣ = \frac{A^\infty_a}{n A^\infty_t}
\]  

where \(n = 1, 2, 3\) for Reactions (1), (2) and (3), respectively. \(A^\infty_a, A^\infty_t\) denote equilibrium specific radioactivity of amine and thiol. Usually only one quantity had