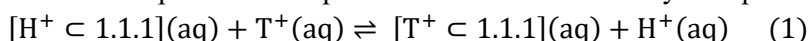# Theoretical Study of Tritium Separation Using [1.1.1] Cryptand

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Keywords: Tritium; Cryptand; Internal Protonation; Isotope Exchange; Density Functional Theory

[1.1.1] cryptand is a bicyclic molecule consisting of two amines bridged by three diethyl ethers. It can accept up to two protons in its cavity and is one of the strongest proton acceptors known to date.[1] It has the potential to separate tritium ions in water by isotopic ion exchange:

$$[H^+ \subset 1.1.1](aq) + T^+(aq) \rightleftharpoons [T^+ \subset 1.1.1](aq) + H^+(aq) \quad (1)$$

where $\subset$ is the inclusion symbol. Unfortunately, the reaction rate of the internal protonation is very slow so that this method cannot be put into practical use on an industrial scale. The rate of the internal protonation becomes faster at higher pH values. The activation energy for the process at pH values from 4.5 to 7.5 is approximately 110 kJ mol^{-1}. The internal protonation has been thought to proceed via external protonation of the amine. This study insists that the internal protonation begins with protonation of the ether oxygen, followed by the proton exchange mediated by a water molecule which transfers a proton to the amine. When an ammonium or phosphoniums are used as proton carriers, they transfer a proton to the amine directly, and decrease the activation energy.

The B3LYP density functional calculations incorporating the PCM solvent effect through the solvent accessible surface were performed with the cc-pVTZ basis set. The equilibrium constant of eq. (1) was evaluated as 2.0 by attaching a hydrogen (tritium) ion to a water cluster consisting of ten molecules. The transition states of the internal protonation when proton carriers are hydronium and ammonium are shown in Figure 1 (a) and (b), respectively. It can be seen that hydronium transfers a proton to the amine and recaptures another proton previously given to the ether oxygen. On the other hand, ammonium transfers a proton to the amine directly. Table 1 shows the Gibbs energies of activation for the proton carriers used. The activation energy tends to decrease as the proton affinity of the carrier increases and the distance between the central atom of the carrier and the proton increases.
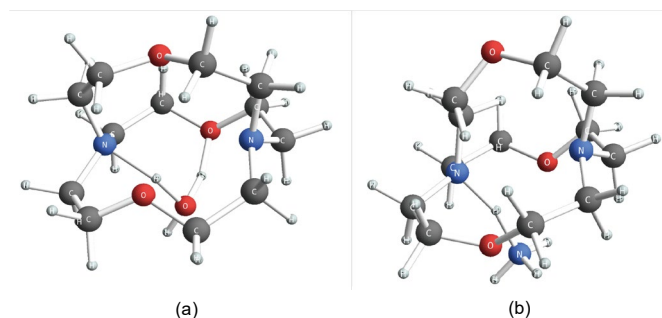

(a)   (b)

Figure 1. Transition state of the internal protonation: (a) hydronium proton carrier, (b) ammonium proton carrier.

Table 1. Proton carrier (a^+) and Gibbs energy of activation.

a^+	$\Delta^{\ddagger}G°$/kJ mol^{-1}
H_3O^+	111.9
NH_4^+	103.2
PH_4^+	96.8
$CH_3PH_3^+$	85.9
$(CH_3)_2PH_2^+$	110.8

1) P. B Smith, J. L. Dye, J. Cheney, J.-M. Lehn, *J. Am. Chem. Soc.* **1981**, *103*, 6044.