

Hydrogen Isotope Equilibration Induced by Tritium Radiation – Ab Initio Approach to Reaction Kinetics

A.B. Sazonov^{a,*}, E.P. Magomedbekov^a

^a*D. Mendeleev University of Chemical Technology of Russia, 9-th Miusskaya sq., Moscow, 125047, Russia*

Simulation of hydrogen isotopes cryogenic distillation when the concentration of tritium is high enough must take into account the isotope equilibration proceeding in “warm” vessels and pipes and resulting in redistribution of the three isotopes between the six molecular hydrogen isotopomers according to the current conditions. The isotope equilibration being induced by tritium beta-radiation is the chain ion-molecule reaction including the stages of the hydrogen ion clusters (H_5^+ , H_7^+ , *etc.*) formation, *intramolecular* isotope exchange and dissociation. Kinetics of this process has been studied experimentally over the decades; however no theory was proposed to describe it quantitatively.

The calculations of potential energy surfaces for the hydrogen ion clusters up to H_{21}^+ have been done by Hartree-Fock and Möller-Plesset (second order) *ab initio* methods with the 6-311**G++ basis set. Molecular parameters and partition functions corresponding to the minima and saddle points on the *intramolecular* isotope exchange pathways have been calculated for the completely tritiated clusters. Then those results were used for estimation of the equilibration rate within the frameworks of Langevine and activated complex theories. Thermalized electrons were considered as the only particles in the gas phase responsible for recombination of the ion clusters. The first-order time constant as a function of temperature, pressure and tritium concentration has been obtained. The numerical data obtained with the Möller-Plesset (but not Hartree-Fock) technique are in good agreement with the experiments.

Our results show that the reaction abilities of different hydrogen ion clusters are not the same. *Intramolecular* isotope exchange in H_5^+ , H_7^+ , and H_9^+ does not require thermal activation; corresponding activation energy for the heavier clusters dominating at low temperatures is about 10 kJ/mol. Thus the equilibration reaction in tritium gas containing additives of other hydrogen isotopes (H or D) completes in few seconds at room and higher temperatures and 0.5 atm while it takes about 10 hours at 77 K and the same pressure. Since all the clusters existing at given conditions participate in the isotope equilibration the pressure dependence of time-constant is quite sophisticated. The equilibration rate is proportional to the square root of tritium molar part in the isotope mixture.