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Study on chemical kinetics of HTO + $H_2 \rightarrow H_2O$ + HT for design of tritium breeding blanket

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ABSTRACT

Understanding the details of chemical kinetics related to the tritium recovery process is necessary to design highly efficient Tritium Extraction System (TES) in the fusion reactors. In the TES, tritium is expected to be released in the form of HTO from the breeder pebbles, and recovered in the form of HT in the helium purge gas containg small amount of hydrogen. The exchange reaction HTO + $H_2 \rightarrow H_2O$ + HT is considered to be one of the important chemical reaction to obtain the tritium in the form of HT in the purge gas flow. In this study, the chemical kinetics of HTO + $H_2 \rightarrow H_2O$ + HT is investigated based on quantum chemistry. Firstly, the potential energy surface will be explored to obtain information of reaction paths and its transition states by using a quantum chemistry calculation software. Then, the reaction rate constant of the exchange reaction is estimated from transition state theory.

1. Introduction

Efficient and reliable tritium recovery process for a breeding blanket is essential for achieving tritium sustainability in a fusion reactor. Tritium Extraction System (TES) is one of main ancillary systems among tritium circuit connected to a solid type breeding blanket which is known as outer fuel cycle contrast to inner fuel cycle having several systems in it such as pumping system, tokamak exhaust processing, isotope separation system, storage and delivery system, fueling system, etc [1].

Main function of TES is to extract bred tritium from the blanket using purge gas that comprises low pressure helium with small amount of hydrogen to facilitate tritium release via isotopic exchange reactions, and to recover tritium before routing to tritium accountancy system then to tokamak exhaust processing in the inner cycle. The bred tritium is known to be released in the form of HTO from breeder to purge gas in a blanket [2], however it is expected to be recovered mainly in the form of HT in TES modules due to presence of hydrogen in purge gas. The exchange reaction HTO + $H_2 \rightarrow H_2O$ + HT is considered to be one of the important chemical reaction to obtain the tritium in the form of HT in the purge gas flow. In this study, the chemical kinetics of HTO + $H_2 \rightarrow H_2O$ + HT is investigated based on quantum chemistry. Firstly, the potential energy surface will be explored to obtain information of reaction paths and its transition states by using a quantum chemistry calculation software. Then, the reaction rate constants of the exchange reaction are estimated from transition state theory.

2. Calculation methods

2.1. *ab initio* electronic structure calculations

The electronic energies of the chemical species and its complex is calculated by Density Functional Theory (DFT) using Gaussian 09 software [3]. As the hybrid functional and the basis set, UB3LYP and cc-pVTZ are employed in the present calculations, respectively.

2.2. Transition state structure searching by MC-AFIR

Transition states on the reaction paths are searched by Multi-Component Artificial Force Induced Reaction (MC-AFIR) method [4] with LUP using GRRM14 program [5]. The AFIR explores a potential energy surface searching for possible stable structures along the so-called AFIR paths. The AFIR path is a barrier less reaction made by applying artificial attractive force. In the MC-AFIR, these AFIR paths are randomly chosen for various positions of the reactants. The accuracy of the AFIR path are improved by applying LUP. The stable structures found in AFIR searching are the approximate transition states (TSs) and local minimums (LMs). They are re-optimized to obtain true TSs and

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LMs for the real reaction path. The potential energy calculations and the structure optimization in these procedures are carried out by Gaussian program that mentioned in the previous sub-section.

In the present study, reaction paths of the $H_2O + H_2 \rightarrow H_2O + H_2$ reaction are searched to determine the transition state structure. Once the transition state structure for the $H_2O + H_2 \rightarrow H_2O + H_2$ reaction is determined, one appropriate hydrogen atom is replaced by a tritium atom, and then structure optimization and frequency analysis are carried out to determine the properties of the transition states structure for $HTO + H_2 \rightarrow H_2O + HT$ reaction. This approach is considered to be valid because isotopes have very similar electronic structures, and mass-difference effects on the equilibrium geometries of the transition state are expected to be negligible as shown in the results for water isotopologues by a non-Born–Oppenheimer approach [6]. The mass-difference effects are taken into account in the frequency analysis to determine the kinetic and the thermal properties.

2.3. Transition state theory reaction rate constant

The TST reaction constants of $HTO + H_2 \rightarrow H_2O + HT$ reaction is deduced by using the KiSThelP [7] package. The conventional expression of TST reaction constant in the unit of cm^3/molecule-s is given by

$$k^{TST} = \sigma \frac{k_b T}{h} \frac{Q^{TS}}{N_A Q^R} \exp\left(-\frac{V^{\ddagger}}{k_b T}\right) \quad (1)$$

where σ is the reaction path degeneracy, k_b the Boltzmann constant, temperature, h the Planck constant, N_A the Avogadro's number, Q^{TS} is the partition function of transition state, and Q^R is the products of partition function of the products, and $V^{\ddagger}$ the activation energy. The KiSThelP package uses the equivalent expression for bimolecular reaction in terms of thermodynamics properties;

$$k^{TST} = \sigma \frac{k_b T}{h} \left(\frac{k_b T}{p^0}\right) \exp\left(-\frac{\Delta G^{\ddagger,0}}{RT}\right) \quad (2)$$

where $\Delta G^{\ddagger,0}$ is the standard Gibbs free energy difference between the reactants and the transitions state in the unit of J/mol. The tunneling effect is considered by multiplying the Wigner's correction factor [8], χ, that is,

$$k^{TST,W} = \chi(T) k^{TST} \quad (3)$$

where

$$\chi(T) = 1 + \frac{1}{24} \frac{h}{k_b T} \mathrm{Im}(v^{\ddagger}) \quad (4)$$

The reaction constants are also calculated by KiSThelP by using the variational transition state theory (VTST);

$$k^{VTST} = \min_s k^{GT}(T, s), \quad (5)$$

where k^{GT} is the generalized transition state rate constant

$$k^{GT} = \sigma \frac{k_b T}{h} \frac{Q^{TS}(T, s)}{N_A Q^R(T, s)} \exp\left(-\frac{V^{\ddagger}(s)}{k_b T}\right), \quad (6)$$

and s is the distance along the reaction path in inertial coordinate. The tunneling correction factor for the VTST rate is calculated based on an Eckart potential energy barrier [9].

The equilibrium constants can be obtained in the form of

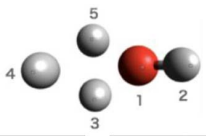
$$K_{eq}(T) = \exp\left(-\frac{\Delta G}{RT}\right). \quad (7)$$

3. Results

3.1. Transition state structure

The AFIR calculations for $H_2O + H_2 \rightarrow H_2O + H_2$ reaction found four approximate TSs and four approximate LMs. By the optimizations of these structures, one approximate TS converged to a stable structure, and the other approximate TSs and LMs are found to be structures on dissociation channel. The optimized structure and the energies of the TS are summarized in Table 1. The frequency analysis for the TS replaced Atom3 by Tritium is also out, and the results are also shown in Table 1. The structure has one imaginary frequency, indicating that the structure is in the saddle point of the potential surface.

Table 1
Optimized structure and properties of TS.

Transition state structure			
		1: O 2: H 3: H or T 4: H 5: H	
		OHHHH	OHTHH
Bond length, Å		**Energies, a.u.**	
R(1,2)	0.9701	Electric	-77.53327	-77.53327
R(1,3)	1.2029	ZPE	0.03086	0.02812
R(1,5)	1.2029	**Vibrational frequency, cm^{-1}**		
R(3,4)	1.1521	1	-2734.1	-2253.5
R(3,5)	1.0956	2	621.6	578.8
R(4,5)	1.1521	3	747.2	620.2
Bond angle, Deg		4	1266.4	1045.1
A(2,1,3)	108.15	5	1507.5	1167.8
A(2,1,5)	108.15	6	1510.9	1410.5
A(1,3,4)	124.49	7	1724.1	1715.5
A(1,5,4)	124.49	8	2429.9	2068.5
Dihedral angle, Deg		9	3737.0	3736.7
D(2,1,3,4)	101.64	**Rotational temperature. K**		
D(2,1,3,5)	99.65	1	18.1	13.7
D(2,1,5,4)	-101.64	2	3.6	2.9
D(1,3,4,5)	-2.01	3	3.5	2.8

3.2. Properties of the reactants

In order to calculate the reaction rate constants by the transition state theory, we need to have the electronic energies and the vibrational frequencies of the reactants. To be consistent, these properties for H_2O, HTO, H_2 and HT is calculated by the same *ab initio* approach as in the calculation for TS. The obtained properties are summarized in Table 2.

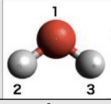
3.3. IRC

Fig. 1 show the IRC paths calculated for the reactions $H_2O + H_2 \rightarrow H_2O + H_2$ and $HTO + H_2 \rightarrow H_2O + HT$ from the obtained TS. The vertical axis is the energy measure from the sum of the electric energies of H_2 and HTO, that is -203.84 kJ/mol. The activation energy for these path is found to be 279.88 kJ/mol. The path for the reaction $HTO + H_2 \rightarrow H_2O + HT$ is slightly broader than that of the $H_2O + H_2 \rightarrow H_2O + H_2$, because the horizontal axis is the mass-weighted reaction coordinate.

3.4. Reaction rate constants by transition state theory

Assuming the nominal temperature and the pressure of the purge gas in the Korean Helium-Cooled Ceramic Reflector (HCCR) Test Blanket Module (TBM) [10], the reaction rate constants for the reaction $HTO + H_2 \rightarrow H_2O + HT$ are calculated for the temperature range from 700 K to 900 K at the pressure of 1 atm. Fig. 2 shows the calculated reaction rate constants as a function temperature. As seen in Fig. 2, the reaction rate constants almost linearly increase as the temperature

Table 2
Properties of H_2O, HTO, H_2 and HT.

	H_2O	HTO	H_2	HT
	 1: O 2: H 3: H or T		 1: H 2: H or T	
Bond length, Å				
R(1,2)	0.9613		0.7429	
R(1,3)	0.9613		-	
Bond angle, Deg				
A(2,1,3)	104.53		-	
Energies, a.u.				
Electric	-76.4598		-1.18000	
ZPE	0.02128	0.01723	0.01007	0.00822
Vibrational frequency, cm^{-1}				
1	1639.6	1363.1	4419.6	3609.7
2	3800.7	2346.5	-	-
3	3901.0	3851.6	-	-
Rotational temperature. K				
1	39.1	32.0	87.2	58.2
2	20.8	9.46	-	-
3	13.6	7.30	-	-

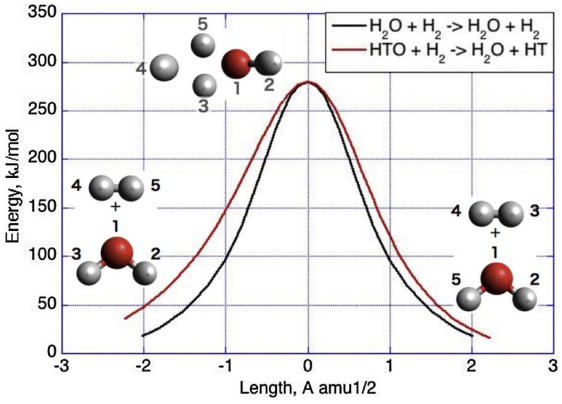


Fig. 1. The calculated IRC path for transition state theory.

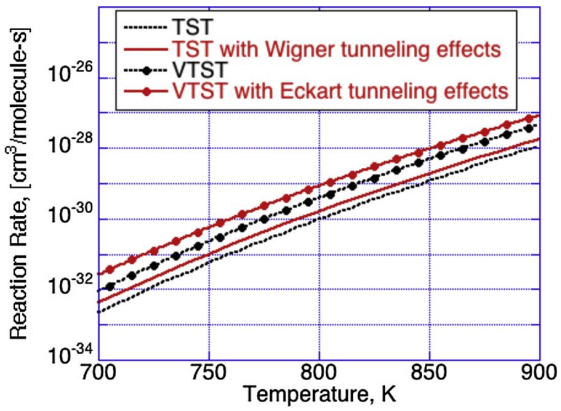


Fig. 2. The obtained reaction rate coefficients.

increase. The reaction rate constant calculated by the variational transition state theory (VTST) is generally greater than that of the original transition state theory(TST).

The tunneling effects correction factor evaluated by Wigner's as well as Eckart's methods are shown in Fig. 3. In both methods, the correction factor decreases when the temperature decrease. The Eckart's method gives higher correction factor compared with the Wigner's method, especially at the lower temperatures. With the tunneling effects, the reaction rate constant in the present temperature range approximately doubles the reaction rate constant.

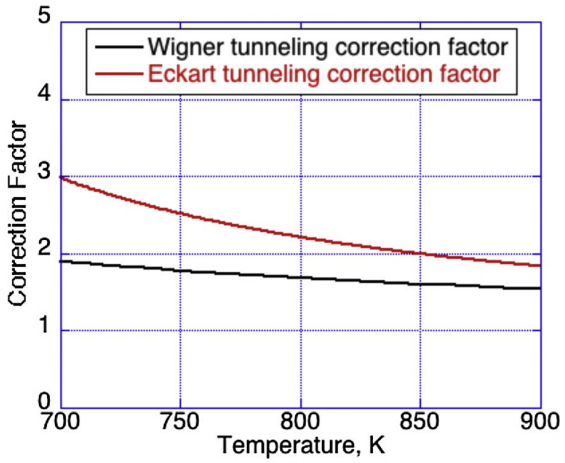


Fig. 3. The tunneling correction factor.

The three parameters for the Arrhenius fitting function are also calculated by the KiSThelP program. The obtained Arrhenius function for the VTST reaction rate constant with the Eckart's correction factor in the temperature range 800 K ± 20% is

$$k_f^{VTST}(T) = 7.8780 \times 10^{-32} T^{5.935} \exp\left(-\frac{232580}{RT}\right). \quad (8)$$

We have taken the same approach for the backward reaction, $H_2O + HT \rightarrow HTO + H_2$, and obtained the Arrhenius function of

$$k_b^{VTST}(T) = 6.3382 \times 10^{-33} T^{6.222} \exp\left(-\frac{225650}{RT}\right). \quad (9)$$

The equilibrium constant in terms of free energy gap between the reactants and the products for the $HTO + H_2 \rightarrow H_2O + HT$ is calculated to be

$$K_{eq}(T) = \exp\left(-\frac{2950}{RT}\right). \quad (10)$$

The equilibrium constant can be also expressed by the ratio of the forward and the backward reaction rate constants. When we take the ratio of Eqs. 8 and 9, we obtain

$$K_{eq}(T) = \frac{k_f}{k_b} = 12.429 T^{-0.287} \exp\left(-\frac{6930}{RT}\right). \quad (11)$$

In Fig. 4, the reciprocals of the present equilibrium constants are compared with the experimental results obtained by Taylor et al. [11] from the partial pressure measurements. Note that the fitting function of Taylor is derived to fit the experimental data in the temperature range from 289.20 K to 576.95 K, while the present fitting function is targeted to represent calculated values for 800 K ± 20%. The present calculations and the fitting functions agree well with the experimental data and its fitting, especially in the temperature range from 400 K to 600 K. It is also shown in Fig. 4 that the fitting functions of Eq. (11) well represents the calculated values of equilibrium constants all over the temperature range. The fitting functions of Eq. (10), which is deduced from the standard Gibbs free energy difference between the reactants and the transitions state at the temperature of 800 K, lose the accuracy in the lower temperature range.

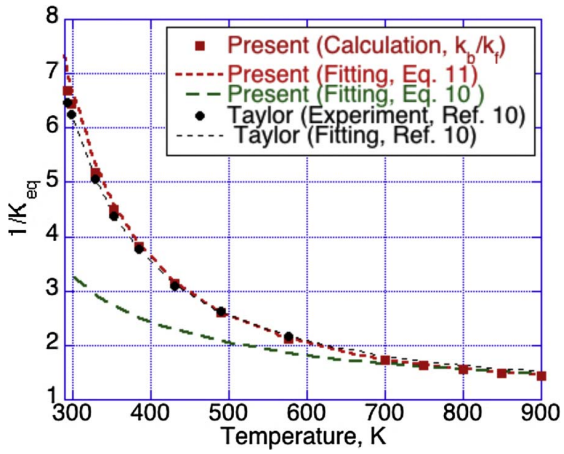


Fig. 4. Comparisons of equilibrium constants.

4. Discussions

The reaction rate constants for the HTO + $H_2 \rightarrow H_2O$ + HT are estimated by the transition state theory, and the fitting expression in the Arrhenius form is given in equation. At 800 K and 1 atm, which is the nominal conditions of the purge gas flow in HCCR TBM, the exchange reaction rate constant is estimated to be 8.5774×10^{-30} cm^3/molecules-s. These small rate is due to the relatively high activation energy for the reaction is 232.58 kJ/mol, that is corresponding to 27,973 K in temperature. Although only the direct exchange reaction by from HTO and H_2 to H_2O and HT are considered in the present study, the possibility of other reaction channels must be studied; i.e., the pre-dissociation of HTO or H_2 molecules into atoms, or the reactions with catalysis. Also, kinetics for other chemical reactions expected to occur in the purge gas flow, for example, reactions related to the other isotopes such as deuterium, must be studied in the future.

5. Conclusions

The reaction paths of HTO + $H_2 \rightarrow H_2O$ + HT are explored by AFIR approach by using GRRM program, and one transition state is successfully discovered. From the obtained transitions state, the reaction rate constant is derived by the transition state theory, and fitted in the Arrhenius form as a function of temperature. For the temperature around 800 K, the reaction rate constant is estimated to be the order of 10^{-30}–10^{-29} cm/molecules-s.

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References

[1] D. Demange, S. Stammler, M. Kind, A new combination of membranes and membrane reactors for improved tritium management in breeder blanket of fusion machines, Fusion Eng. Des. 86 (2011) 2312–2316.

[2] F. Franza, L.V. Boccaccini, A. Ciampichetti, M. Zucchetti, Tritium transport analysis in HCPB DEMO blanket with the FUS-TPC code, Fusion Eng. Des. 88 (2013) 2444–2447.

[3] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc, Wallingford, CT, 2016.

[4] S. Maeda, K. Morokuma, A systematic method for locating transition structures of a + B → X type reactions *J. Chem. Phys.*, 2010, 132, 241102 (4 pages); S. Maeda , K. Morokuma Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms *J. Chem. Theory Comput.*, 2011, 7, 2335-2345.

[5] S. Maeda, Y. Harabuchi, Y. Osada, T. Taketsugu, K. Morokuma, K. Ohno, see http://grrm.chem.tohoku.ac.jp/GRRM/ (accessed date DAY MONTH, YEAR).; S. Maeda, K. Ohno, K. Morokuma, Systematic Exploration of the Mechanism of Chemical Reactions: the Global Reaction Route Mapping (GRRM) Strategy by the ADDF and AFIR Methods *Phys. Chem. Chem. Phys.*, 2013, 15, 3683-3701.

[6] A.G. Császár, G. Czakó, T. Furtenbacher, J. Tennyson, V. Szalay, S.V. Shirin, N.F. Zobov, O.L. Polyansky, On equilibrium structures of the water molecule, J. Chem. Phys. 122 (2005) 214305.

[7] Canneaux, F. Bohr, E. Hénon, KiSThelP: a program to predict thermodynamic properties and rate constants from quantum chemistry results, J. Comp Chem. 35 (2014) 82–93.

[8] E. Wigner, Über das Überschreiten von Potentialschwellen bei chemischen Reaktionen, Z. Für Phys. Chem. 19B (1932).

[9] C. Eckart, The penetration of a potential barrier by electrons, Phys. Rev. 35 (1930) 1303–1309.

[10] M.-Y. Ahn, S. Cho, D.W. Lee, C.W. Lee, K.I. Shin, D.Y. Ku, Y.-H. Park, C.-S. Kim, I.-K. Yu, Y.O. Lee, E.H. Lee, H.G. Jin, S.-K. Kim, Design change of Korean HCCR TBM to vertical configuration, Fusion Eng. Des. 88 (2013) 2284–2288.

[11] J.F. Black, H.S. Taylor, Equilibrium in hydrogen water systems containing tritium, J. Chem. Phys. 11 (1943) 395–402.