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Isotope exchange reaction in tritium-contaminated vacuum pump oil: mechanism and HTO effect†

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As radioactive wastes, contaminated vacuum pump oils from tritium-processing facilities are challenging to dispose of. In this study, we investigated the mechanism of the tritium–hydrogen (T–H) exchange reaction between the tritiated water (HTO) and many typical organic molecules in vacuum pump oil using a density functional theory (DFT) method. The T–H exchange reaction could proceed with two mechanisms, the direct T–H exchange mechanism and the addition–elimination T–H exchange mechanism. The calculation indicates that the direct T–H exchange mechanism is kinetically favored. The HTO molecule is not only a reactant, but also acts as the proton shuttle in the transition state. The number of HTO molecules participating in the reaction is determined by the formation of the stable six-membered ring proton migration transition state. The T–H exchange reaction is selective, and molecules with COOH and OH groups preferentially undergo hydrogen exchange with HTO. In the case of multiple possible products, the calculations correctly predicted the predominant product. The results here will provide guidance for improving the associated decontamination process and reducing the environmental impact.

1 Introduction

In tritium-related facilities, a large amount of tritium-contaminated pump oil is produced by vacuum pumps,[1] mainly through the tritium–hydrogen (T–H) isotope exchange reaction.[2] The main components of vacuum pump oil are hydrocarbons, such as alkanes, cycloalkanes, and aromatic compounds,[1] plus small amounts of water. When tritium interacts with the water, highly toxic tritiated water (HTO) would be formed in pump oil. The formed HTO then easily reacts with the organic components to generate more toxic organic tritium-containing compounds. The resulting radioactive waste is expensive and very difficult to dispose. Therefore, it is essential and urgent to develop economic and efficient methods to dispose/decontaminate these tritium-containing wastes.

After exposure to pump oil, tritium may also react with the hydrocarbons to directly form tritiated hydrocarbons.[3] In the presence of oxygen, tritium and hydrocarbons may further undergo radiochemical oxidation to produce peroxide and hydroperoxide radicals. These radicals then react with other organic molecules to form stable tritiated oxides, such as alcohols, carbonyl compounds and carboxylic acids. In the presence of HTO, various organic tritium compounds would be formed between HTO and the organic species through the T–H exchange reaction. In order to develop scientific and effective treatment methods for the tritiated waste pump oil, it is crucial to confirm the chemical forms of tritium in the oil following T–H exchange.

Several groups have made great contributions regarding the interaction of tritium with oil. Takeishi *et al.*[1] demonstrated that pump oil can be contaminated by bubbling with trace tritium gas or tritiated water vapor, and that bubbling with gases containing non-tritiated water vapor is an effective decontamination method. Sazonov and Magomedbekov *et al.* established the chemical forms of tritium in vacuum pump oil and proposed the effective treatment of tritium-contaminated oil through isotope exchange.[3,4] In contrast to these experimental investigations, however, theoretical modeling of the T–H isotope exchange reaction in tritium-contaminated pump oil is rare in the literature.

Previously, we reported theoretical investigations concerning the mechanism of the T–H exchange reaction between T_2 and several typical organic molecules in vacuum pump oil and calculated the reaction rates to form different tritiated products.[5] However, the mechanism of the T–H exchange reaction with HTO is still poorly understood. Furthermore, HTO creates hydrogen bonding interaction in the system, therefore, the reaction of organic molecules would be different and likely more complex from that with T_2.

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While there are considerable experimental studies of the T–H isotope exchange process, molecular level knowledge of the T–H exchange reaction between HTO and the components of pump oil is still lacking. Furthermore, previously investigations have indicated that such isotope exchange is selective for the different functional groups of the organic compounds. However, the reactivity of the organic molecules with different functional groups with HTO is unclear. A better understanding of the T–H exchange process involving HTO, and the chemical states of tritium in pump oil after this reaction would give guidance for the detritiation of the contaminated oil.

Herein, we used density functional theory (DFT) to study the gas-phase T–H exchange reaction between HTO and several organic molecules representative of the main constituents of pump oil. We examined the reactivity of these organic molecules and the selectivity of the products. Furthermore, we clarify the impact of HTO for the T–H exchange process in this paper.

2 Computational details

Among the correlated functional theories, the hybrid meta exchange–correlation M06-2X functional performs well for systems with weak interactions,[6] and previous investigations indicate that M06-2X method could provide highly accurate energies.[7] All calculations were carried out using the Gaussian 09 program.[8] All stationary points and transition states (TSs) on the potential energy surface (PES) were optimized using M06-2X method with the 6-311++G(d,p) basis set.[9] Zero-point vibrational energy (ZPVE) corrections were applied to the relative energies. The vibrational frequencies were obtained at the same level, and the characterized species were either a minimum (no imaginary frequency) or a transition state (unique imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed to further confirm that the optimized transition state (TS) correctly connects the relevant reactant and product.

An energy decomposition analysis (EDA) of the T–H exchange reaction with one or two HTO molecules presented was performed.[10] The activation barrier of one step is divided into two parts: the deformation energy ΔE_d and the interaction energy ΔE_{int}. The deformation energy ΔE_d is the energy required to deform the fragments into the geometries they have in the TS. The interaction energy between the fragments is obtained by the activation barrier of that step to minus the deformation energy. All the EDA energies were obtained by frequency calculations at the M06-2X/6-311++G(d,p) level of theory on the geometries optimized.

3 Results and discussion

Our previous study suggests that the ability of T–H exchange for aromatic compounds is similar to that for non-aromatic ones.[5] Thus, we only choose a variety of non-aromatic molecules that are representative of the main components in pump oil. Our calculations indicate that the T–H exchange between the organic molecules and HTO mostly proceed through the direct T–H exchange mechanism. For molecules with unsaturated double bonds, the reaction may proceed through the addition–elimination mechanism.

Effect of HTO

Numerous studies have proposed that the water molecule could facilitate hydrogen transfer reactions through relaying proton via the six-membered ring hydrogen migration TS.[11] In the case of HTO, the T–H exchange TS could be four- or six-membered ring containing one or two HTO, respectively.

We first use methane, the simplest hydrocarbon, to investigate whether one or two HTO molecules participate in this reaction. The optimized structures and their relative energies calculated at the M06-2X/6-311++G(d,p) level for the T–H exchange reaction of CH_4 are given in Fig. 1.

The reaction starts with HTO attacking the C atom of CH_4. Subsequently, T–H exchange between HTO and CH_4 occurs via hydrogen migration, generating the products CH_3T and H_2O. The hydrogen migration processes could involve either one or two HTO molecules. For the first case, the transition state (labeled $TS_{CH_4–HTO}$) is a four-membered ring containing one HTO. The vibrational mode of $TS_{CH_4–HTO}$ involves the T1 atom moving toward the C1 atom, while H1 atom simultaneously moves toward the O1 atom. When there are two HTO molecules in the system, the hydrogen migration occurs via a six-membered ring TS. The six-membered ring TS has two possible configurations, $TS_{CH_4–2HTO-1}$ and $TS_{CH_4–2HTO-2}$, with the hydrogens in the two HTO positioned in the cis- and trans-conformations with respect to the six-membered ring. The whole hydrogen migration process includes the migration of T1 to C1, T2 to O1 and H1 to O2. The net result of this three proton-transfer process is the generation of CH_3T, together with H_2O and HTO.

The relative energy of $TS_{CH_4–2HTO-2}$ (51.3 kcal mol^{-1}) is slightly lower than that of $TS_{CH_4–2HTO-2}$ (52.2 kcal mol^{-1}), suggesting the trans-conformation has less steric hindrance. The relative energy of $TS_{CH_4–HTO}$ (75.5 kcal mol^{-1}) is much higher than those of $TS_{CH_4–2HTO-1}$ and $TS_{CH_4–2HTO-2}$. Therefore, having
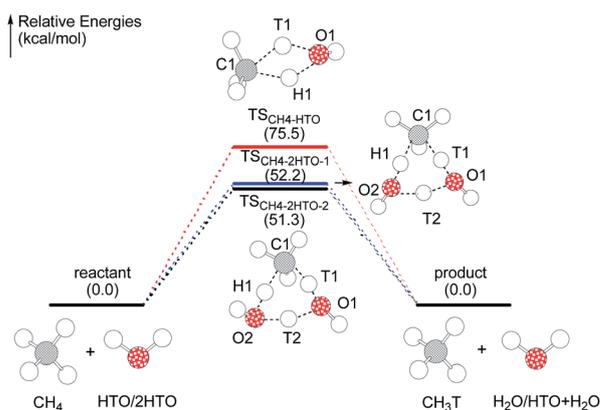

Fig. 1 Reaction paths of T–H exchange of CH_4, and the corresponding optimized structures along the reaction path. Red lines: the path involving one HTO; blue and black lines: the paths involving two HTOs. $TS_{CH_4–2HTO-1}$ and $TS_{CH_4–2HTO-2}$ are TSs positioned in the cis- and trans-conformations, respectively. Relative energies (kcal mol^{-1}) of the species with regard to the reactants are shown in parentheses.

another HTO molecule in the reaction system could facilitate the H–T exchange reaction through relaying the proton *via* a six-membered ring hydrogen migration TS containing two HTO molecules, instead of a four-membered ring involving one HTO. In other words, the H–T exchange reaction preferentially occur through the six-membered ring hydrogen migration TS with two participating HTO molecules. Moreover, in the six-membered ring, the configuration with the hydrogens in the two HTO positioned in the *trans*-conformation is favored.

Previous investigations concerning the role of water in the hydrogen migration process proposed that such a remarkable decrease in the relative TS energy could be ascribed to the reduced ring strain upon changing from four- to six-membered ring TS.[11,12] In order to discuss the differences with one or two HTO molecules present in the reaction system and interpret the impact of HTO, the energy decomposition analysis (EDA) of this process with one or two HTO molecules was performed.[10] The contributions to the interaction energy and deformation energy of the three fragments (CH_4, HTO_1 and HTO_2) during the formations of the TSs are listed in Table 1. Compared with the four-membered ring transition state $TS_{CH_4–HTO}$, the reaction with two HTO molecules involves a less strained six-membered ring transition state $TS_{CH_4–2HTO-2}$. The more relaxant orientations of the fragments in $TS_{CH_4–2HTO-2}$ give enough chances for the fragments to interact with each other, resulting in stronger interaction between them. Therefore, the interaction energy between the fragments in $TS_{CH_4–2HTO-2}$ is 45 kcal mol^{-1} lower than that in $TS_{CH_4–HTO}$. The deformation energy of CH_4 and HTO_1 in $TS_{CH_4–HTO}$ are 8.8 kcal mol^{-1} lower and 14.4 kcal mol^{-1} higher than those in $TS_{CH_4–2HTO-2}$, respectively. However, the presence of the second HTO molecule (HTO_2) has a 22.4 kcal mol^{-1} deformation energy, resulting in the higher deformation energy of $TS_{CH_4–2HTO-2}$ than that of $TS_{CH_4–HTO}$ (61.4 *vs.* 82.2 kcal mol^{-1}). Although the deformation energy of $TS_{CH_4–HTO}$ is lower than that of $TS_{CH_4–2HTO-2}$, the much lower interaction energy overwhelms this unfavorable deformation energy, resulting in the higher activation barrier of the reaction with one HTO molecule. Therefore, the presence of the second HTO molecule makes the orientations of the fragments in $TS_{CH_4–2HTO-2}$ more suitable for them to interaction with each other, which can overwhelm the deformation energy it brings, and it may be the main reason for the lower activation barrier of this pathway.

For molecules with adjacent carbonyl and alkyl groups, such as CH_3COCH_3, CH_3CHO, and CH_3COOH, it is known that the six-membered ring TS could only contain one HTO, since the carbonyl group would also participate in the TS. We chose to study CH_3COCH_3, in which all the hydrogen atoms have the same bonding. For the T–H exchange reaction path involving

one HTO molecule, the calculated potential energy surface at the M06-2X/6-311++G(d,p) level and the corresponding optimized structures are given in Fig. 2.

As shown in Fig. 2, the reaction contains two steps. First, the proton migrates from the methyl group to carbonyl group *via* a six-membered ring TS involving one HTO molecule. A second HTO is no longer required since the carbonyl group also participates in the TS. The whole proton migration process includes the migration of H1 to O1 and T1 to O2. The net result of this one-step, two-proton-transfer process generates the intermediate CH_2=COT–CH_3 as well as H_2O. In the second step, the proton migrates from the hydroxyl group to the alkene group *via* a six-membered ring TS involving another HTO molecule. This process includes the migration of T1 to O1 and T2 to C1, resulting in the generation of the product CH_3-$COCH_2T$. The relative TS energies of the two steps, $TS1_{CH_2=COT-CH_3}$ and $TS2_{CH_3COCH_2T}$, are calculated to be 32.5 kcal mol^{-1} and 31.3 kcal mol^{-1}, respectively.

From the above two examples, it is clear that the number of HTO molecules participating in the reaction is determined by the formation of the stable six-membered ring proton migration TS. The HTO molecules are not only a reactant, but also act as the proton shuttle in the TS. For molecules without the unsaturated carbonyl group, such as CH_4, C_2H_4, and C_2H_5OH, two HTO molecules would participate in the T–H exchange process *via* a six-membered ring TS. For those containing the carbonyl group, the carbonyl group could be part of the TS, thereby requiring only one HTO molecule in the TS.

It should be emphasized that more HTO molecules participated in the direct T–H exchange process may further decrease the transition state energy since the smaller ring strain, but too
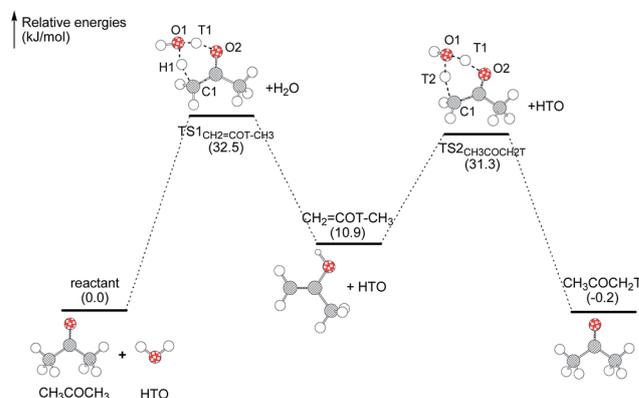

Fig. 2 Reaction path of T–H exchange of CH_3COCH_3, and the corresponding optimized structures along the reaction path.

Table 1   EDA energies of the T–H exchange reaction with one or two HTO molecules present. All energies are given in kcal mol^{-1}

| Process | $\Delta rE^{\neq}$ | ΔE_d of fragment | | | ΔE_d | ΔE_{int} |
		CH_4	HTO_1	HTO_2		
$CH_4 + HTO_1 \rightarrow TS_{CH_4-HTO}$	75.5	32.6	28.8	—	61.4	14.1
$CH_4 + HTO_1 + HTO_2 \rightarrow TS_{CH_4-2HTO-2}$	51.3	41.4	18.4	22.4	82.2	−30.9

much HTO participated in would cause the chain is too long and less stable. Thus, determining the appropriate number of HTO is a very complicated problem. The further studies on how many HTO molecules are needed in the T–H exchange reaction are currently under investigation.

Direct T–H exchange mechanism

Next, we consider organic reactants containing different types of hydrogen, since they can form multiple tritiated products when the T–H exchange occurs at different positions. The T–H exchange reaction pathways of CH_4, C_2H_6, C_3H_8, C_2H_4, C_3H_6, C_2H_5OH, CH_3CHO, CH_3COCH_3 and CH_3COOH are presented in Fig. 3, together with the optimized structures calculated at the M06-2X/6-311++G(d,p) level.

As shown in Fig. 3, these reactions occur through a six-membered ring hydrogen migration TS assisted by two HTO molecules. For molecules with the carbonyl group (CH_3CHO, CH_3COCH_3 and CH_3COOH), the hydrogen migration would occur between the carbonyl group and neighboring group with saturated hydrogen (such as methyl or hydroxyl groups) through a six-membered ring TS assisted by one HTO molecule, forming an enol structure. Thus, there exists an additional keto–enol tautomerism TS including one HTO molecule.

The T–H exchange TS determines the reactivity of the hydrogen in the functional groups of organic molecules. In Fig. 3, all the relative TS energies for alkanes are above 50.0 kcal mol^{-1}, while those of alkenes are below 50.0 kcal mol^{-1}. Therefore, the activity of T–H exchange is in the order of alkene

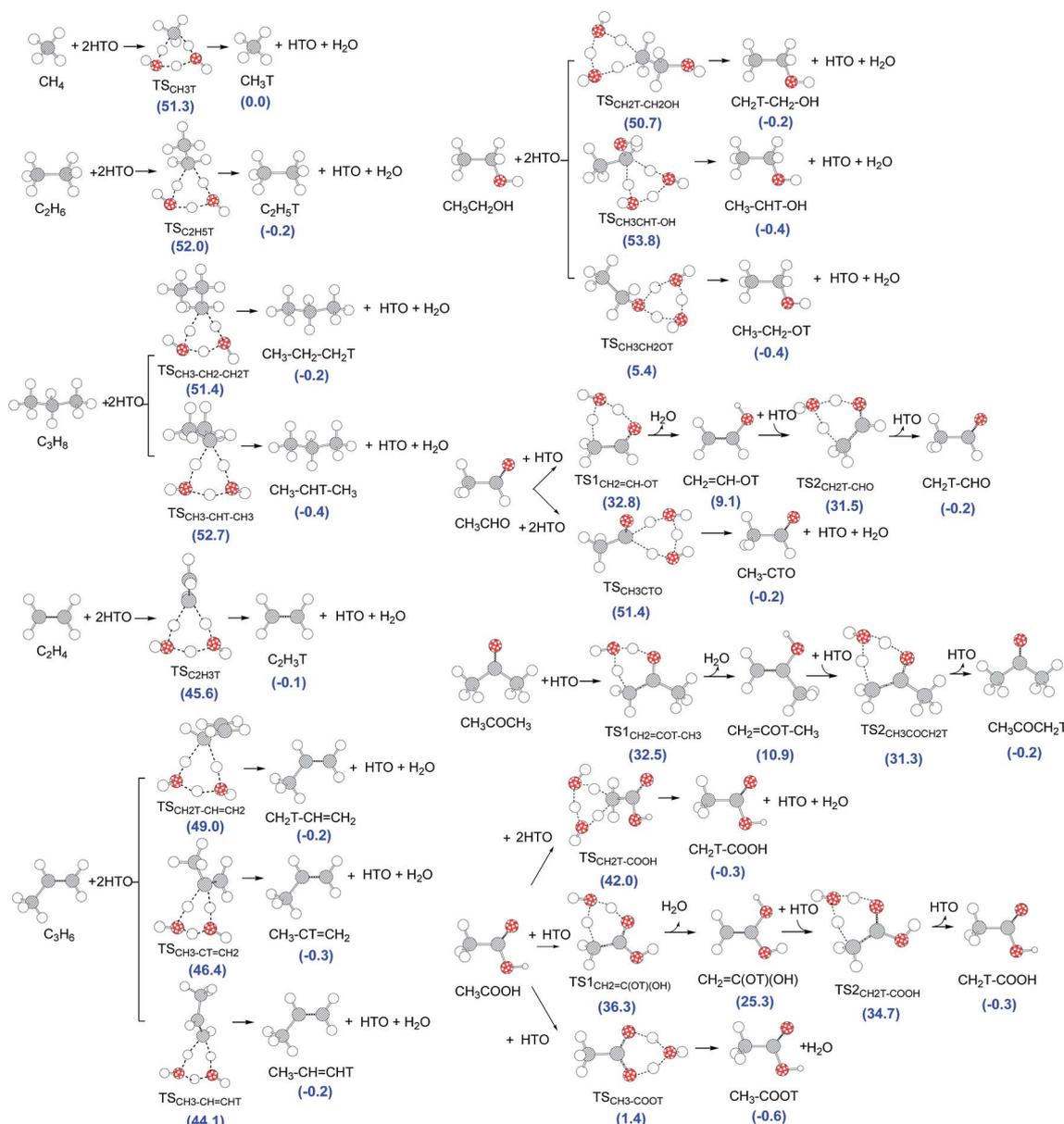**Fig. 3** Direct T−H exchange reaction pathways of CH_4, C_2H_6, C_3H_8, C_2H_4, C_3H_6, CH_3CH_2OH, CH_3CHO, CH_3COCH_3 and CH_3COOH. Relative energies (kcal mol^{-1}) of the corresponding species relative to the reactants are shown in parentheses.

> alkane. For oxygen-containing molecules, the energies for non-oxygenated hydrogens (*i.e.*, CH_3 and CH_2 in CH_3CH_2OH) are higher than 50.0 kcal mol^{-1}, while that for the methyl hydrogen in CH_3COOH is higher than 35.0 kcal mol^{-1}. However, the TS energy of the COOH group (1.4 kcal mol^{-1}) is lower than that of the OH group (5.4 kcal mol^{-1}), and both are much lower than those of alkyl groups. Thus, T–H exchange occurs more easily in the OH and COOH groups of alcohol and carboxylic acid, respectively. This makes sense because tritium readily replace the most active hydrogen in an organic molecule.[4] For the aldehyde, the T–H exchange TS of CH_3 occurs through two consecutive hydrogen migrations each with a six-membered ring TS, and the relative energies of these TSs are lower than that of CHO. Therefore, the reaction of aldehydes preferentially occur in the CH_3 group. Moreover, for the ketone, the relative TS energy for CH_3 is 32.5 kcal mol^{-1}, almost the same as that of aldehyde. Thus, assuming the direct T–H exchange mechanism, the functional groups are ordered as follows in terms of their ability for T–H exchange: CH_3COOH > CH_3CH_2OH > $CH_3CHO \approx CH_3COCH_3$ > alkene > alkane.

Addition–elimination T–H exchange mechanism

For unsaturated organic molecules, there is another T–H exchange mechanism of addition–elimination. This mechanism is composed of two steps: (1) the addition of HTO to the unsaturated bond in the organic molecule, and (2) the elimination of one H_2O from various hydrogen positions. If the elimination of H_2O forms an enol structure, the aforementioned keto–enol tautomerism would occur assisted by another HTO. The addition–elimination T–H exchange mechanism always involves more than one TSs, and the one with the highest relative energy, namely the rate-determining step, determines the reactivity.

The optimized structures of addition–elimination T–H exchange reaction pathways of C_2H_4, C_3H_6, CH_3CHO, CH_3COCH_3 and CH_3COOH are presented in Fig. 4. From the calculation results, T–H exchange through the double bond of alkene is slightly easier than through the CHO group in aldehyde or the carbonyl group in ketone, and the latter two have almost the same level of reactivity. For the aldehyde and ketone, the relative TS energies of the elimination step are much higher than those of the addition step and keto–enol tautomerism TS. Therefore, the step of H_2O elimination in the addition–elimination T–H exchange mechanism determines the ability of T–H exchange in aldehyde and ketone. The T–H exchange in the COOH group is the easiest, compared to the other unsaturated groups studied here. According to the calculations, the ability of T–H exchange *via* the addition–elimination exchange mechanism is ordered as CH_3COOH > $CH_3COCH_3 \approx CH_3CHO$ > alkene. It is noted that after adding HTO to CH_3COOH, the intermediate CH_3–$COT(OH)_2$ could not undergo the elimination process, since the strongly electronegative O atom retains the hydrogen. Thus, after the formation of CH_3–$COT(OH)_2$ by addition, the hydrogen exchange proceeds through relaying proton *via* the six-membered ring TS.

It should be emphasized that peroxides could also be formed when HTO adds to molecules with oxygen-containing groups. However, the calculated reaction paths of CH_3CHO, CH_3COCH_3, and CH_3COOH in Fig. 4 indicate that the TS for forming the peroxide and the corresponding intermediate are unstable, with rather high relative energies for the conditions in experiments. Thus, these paths are no longer considered.

Compared to the direct T–H exchange mechanism, it is clear that the relative energies of the addition or elimination steps are higher since these processes have four-membered ring TS, while the direct exchange always occurs through proton relay *via* six-membered ring TS, facilitated by one or two HTO molecules. The remarkable energy difference is attributed to the higher strain in the four-membered ring TS.

In summary, according to the calculations involved in the direct and the addition–elimination T–H exchange mechanisms, we conclude that the ability of T–H exchange is ordered as CH_3COOH > CH_3CH_2OH > $CH_3CHO \approx CH_3COCH_3$ > alkene > alkane, and the reaction preferentially occur through the direct T–H exchange mechanism. Tritiated water more easily exchanges the most mobile hydrogen atoms in organic molecules, in other words, molecules with COOH and OH groups most readily exchange hydrogen with the HTO. These results are somewhat different from our previous studies of T_2 with organic molecules in the T–H isotope exchange reaction,[5] which could proceed *via* either the direct or the hydrogenation–dehydrogenation mechanisms, according to the types of the organic molecules.

Products distribution

According to the Boltzmann distribution, the selectivity of the products are predicted. As mentioned above, the direct mechanism is kinetically favored (with lower relative TS energy) for T–H exchange reactions between HTO and these molecules. The corresponding product selectivities for CH_4, C_2H_4, C_2H_5OH, CH_3CHO, CH_3COCH_3, and CH_3COOH were calculated. The products and the calculated selectivity from the direct T–H exchange mechanism are listed in Table 2.

Reactants containing one type of hydrogen, such as CH_4, C_2H_4, and CH_3COCH_3 have the single product.

Reactants containing different types of hydrogen, such as C_2H_5OH, CH_3CHO, and CH_3COOH have competitive products. In the case of C_2H_5OH, there are three different products. As shown in Table 1, the calculated selectivity for CH_3CH_2OT is almost 100.0%, while those for CH_2TCH_2OH and CH_3CHTOH are almost zero. In other words, the CH_3CH_2OT + H_2O formation is kinetically predominant, whereas the other two products can be ruled out.

Similarly, the reactant CH_3CHO can form either CH_2TCHO or CH_3CTO. The selectivity of CH_2TCHO is calculated to be 100.0%, while the other is almost zero. Thus, the CH_2TCHO is the predominant product, while that for CH_3CTO formation is so small to be negligible.

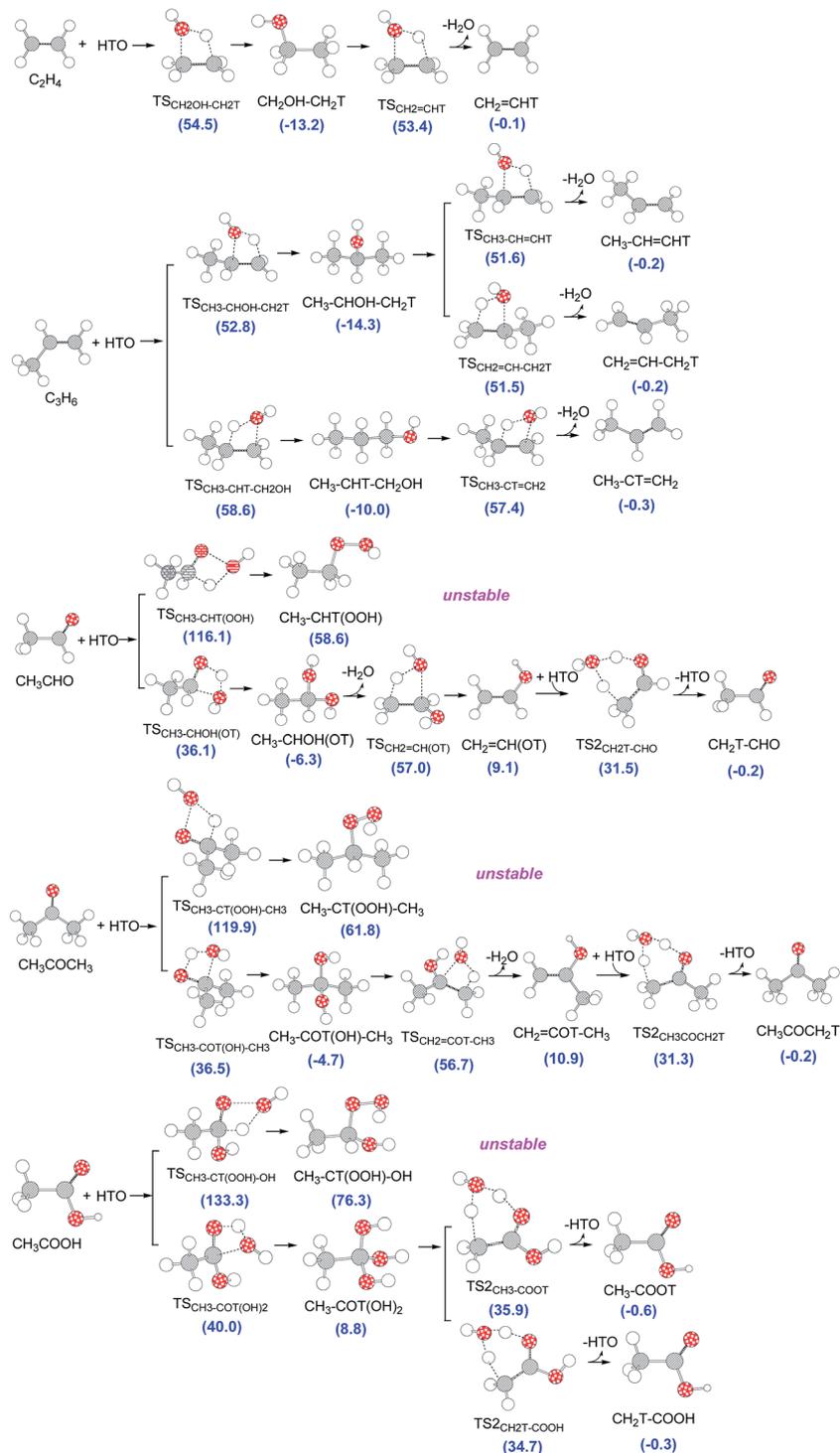Finally, the reactant CH_3COOH leads to the formation of CH_2TCOOH and CH_3COOT. The selectivity of CH_3COOT is

Fig. 4 Addition–elimination T–H exchange reaction pathways of C_2H_4, C_3H_6, CH_3CHO, CH_3COCH_3, and CH_3COOH. Relative energies (kcal mol^{-1}) of the corresponding species relative to the reactants are shown in parentheses.

calculated to be 100.0%, while the others is almost zero. Thus, the CH_3COOT is the predominant product.

It is helpful to handle the tritium-contaminated vacuum pump oil using more scientific and proper methods by confirming the chemical forms of tritium existed in the oil. As mentioned above, in the presence of HTO, molecules with COOH and OH groups are most readily exchanged with HTO, and CH_3CH_2OT and CH_3COOT might be the main components in the pump oil. Using the strong acidic or basic reagents to react with the tritiated compounds might be the efficient method to recover tritium and decrease the radiation hazard.

Table 2 Products and selectivities (%) of the different molecules in the direct T–H exchange reaction mechanism

Species	Product	Selectivity (%)
CH_4	CH_3T	—
C_2H_4	C_2H_3T	—
C_2H_5OH	CH_2TCH_2OH	≈ 0
	CH_3CHTOH	≈ 0
	CH_3CH_2OT	≈ 100
CH_3CHO	CH_2TCHO	≈ 100
	CH_3CTO	≈ 0
CH_3COCH_3	CH_3COCH_2T	—
CH_3COOH	CH_2TCOOH	≈ 0
	CH_3COOT	≈ 100

4 Conclusions

The mechanism of the T–H exchange between HTO and many typical organic molecules in pump oil has been investigated theoretically. The reactivity of different reactants and the selectivity of the products were also examined. The major conclusions are the following:

(1) T–H exchange reaction between HTO and the organic molecules in pump oil could proceed with two different mechanisms: the direct and the addition–elimination T–H exchange mechanisms. The calculations indicate that the direct T–H exchange mechanism is kinetically favored.

(2) The HTO molecule is not only a reactant, but also acts as the proton shuttle in the TS. For molecules without the unsaturated carbonyl group, the T–H exchange could easily occur *via* a six-membered ring hydrogen migration TS including two HTO molecules, instead of the four-membered ring TS with only one HTO molecule. For those containing the carbonyl group, the carbonyl group could be part of the TS, thereby requiring only one HTO molecule in the TS.

(3) The T–H exchange is selective. Molecules containing the COOH and OH groups exchange with the HTO more easily. The predominant products for reactants C_2H_5OH, CH_3CHO, and CH_3COOH are CH_3CH_2OT, CH_2TCHO, and CH_3COOT, respectively.

Acknowledgements

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