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Ab initio calculations on the mechanism of isobutane and 2-butene alkylation reaction catalyzed by hydrofluoric acid

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Abstract

Ab initio method was employed to determine the mechanism of alkylation reaction of 2-butene with isobutane. The results indicated that 2-butene is rapidly protonated to form *sec*-butyl carbonium ion, which then reacts with isobutane to form *tert*-butyl carbonium ion. The resulting carbonium ion is then deprotonated to form isobutene that reacts rapidly with *tert*-butyl carbonium ion to form trimethylpentane (TMP) carbonium ion. Finally, the TMP^+ carbonium ion is converted to TMP via the hydride transfer process. The transition states of the interactions were obtained by using the SCAN method (a calculation key word for potential energy surface) first and then the intrinsic reaction coordinates were traced using the Gaussian program. In addition, the energy changes and geometric parameters of the interactions were analyzed. The computed results indicated that the energy barriers are close to or less than zero for the interaction of isobutane with protonated 2-butene or for the interaction of *tert*-butyl carbonium ion with isobutene, suggesting rapid reaction steps of the carbonium ions. The 2,2,3-TMP is kinetically controlled, while the formation of 2,2,4-TMP is controlled by reaction equilibrium. The calculated results were in good agreement with the experimental results.

Keywords: Isobutane; 2-Butene; Alkylation; Mechanism; Molecular simulation

1. Introduction

One of the important processes used in petroleum refinery industry is the butene alkylation of isobutane for producing alkylated gasoline. The current commercial alkylation processes are carried out using sulfuric or hydrofluoric acid as catalysts [1–3]. It is well known that 2,2,3-trimethylpentane (TMP) is the desirable compound in alkylated products. Researches on the reaction have been going on, and some interesting results have been reported [4–9]. Thomson et al. [4] have studied the batchwise gas-phase alkylation of isobutane with 1-butene at 80 °C catalyzed by sulfated zirconia or beta zeolites with different molar SiO_2/Al_2O_3 ratios. It was found that the yield of TMP is greatly correlated to the activity of the hydride transfer reaction of the intermediates. Hommeltoft and co-workers [5] carried out a simulation on the decomposition of TMP and observed that the high concentration isobutene stabilizes TMP in the reaction mixture, which is beneficial to the formation of TMP.

Recently, ionic liquid-catalyzed alkylation of isobutane with 2-butene has been reported [6–9]. However, these ionic liquids are limited to either the supports impregnated with pre-formed ionic liquids as catalysts [8,9] or imidazolium based chloroaluminate species [6,7]. Furthermore, ionic liquids are different from the conventional liquid strong acids and the mechanism for its catalyzing isobutane alkylation reaction with butene is suspending.

Regardless of heterogeneous or homogeneous reactions, the alkylation reaction process is complex because of the simultaneous reactions including olefin polymerization and cracking. Nevertheless, the key reaction mechanism involves rapid protonation of 2-butene to form *sec*-butyl carbonium ion followed by the hydride transfer process of isobutane to form *n*-butane and *tert*-butyl carbonium ion. The resulting *tert*-butyl carbonium ion reacts rapidly with 2-butene to produce TMP^+. The TMP^+ ion is converted to TMP via hydride transfer process and *tert*-butyl carbonium ion will return to the reaction cycle [10–17].

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Hydride transfer between alkanes and alkylcarbenium ions is the elementary step responsible for chain propagation of many hydrocarbon transformations catalyzed by acids. The postulated mechanism has not been validated due to the difficulty in detecting the intermediates under the rigorous reaction conditions and the complexity of the reaction system. The main objective of this work is to localize the stable intermediates, that is to say, the tight complexes, through which the hydride transfer reaction occurs. Hydrofluoric acid is chosen as the catalyst because the database could be established on the basis of the previous reports. Furthermore, this work can be extended to other systems in which the presence of the novel acid catalysts (for example ionic liquids) can be explicitly taken into account in the future. Therefore, it is of vital significance to test the validity of the *ab initio* theory for studying this type of reaction mechanism.

2. Calculation methods

One of most frequently used methods in density functional theory is B3LYP [18–21]. However, the calculated orbital energy values deviate far from the real ones. In principle, we can obtain the accurate values as long as the high level of basis set of the *ab initio* method based on Hartree–Fock (HF) is used. The common point of the two methods is that both of them satisfy the variational principles. Herein, this is done by comparing the results obtained at the different levels (B3LYP/6-31 + G* or HF/6-311G**) with the experimental data previously reported. So the full geometry optimization for the materials involved in these reaction steps was recounted at HF/6-311G** level in this paper. All the calculations were performed with the Gaussian 03W program system [22].

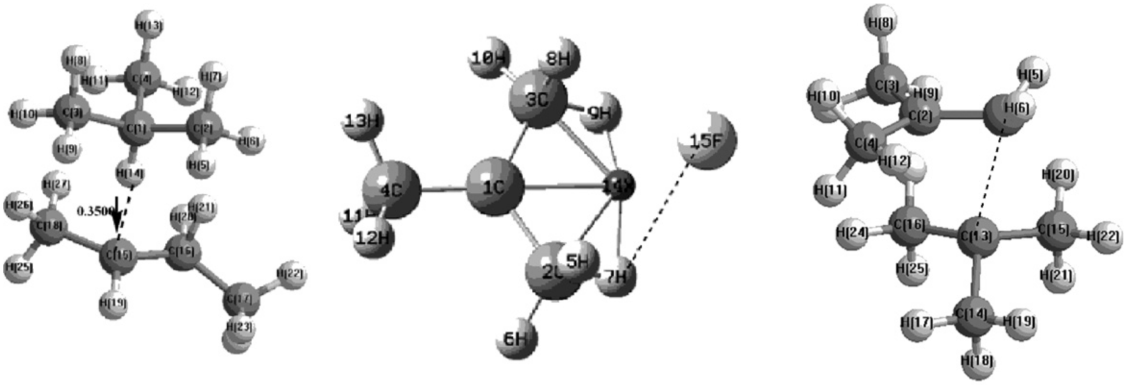
The ground states, such as isobutane and 2-butene molecules and the relevant carbonium ions, were calculated and their net atomic charges and frontier molecular orbitals were analyzed. The non-controlling step of the rapid protonation of 2-butene was omitted, and the three reactions of the protonated 2-butene with isobutane (see model 1-1 in Fig. 1) to describe the process of the formation of *tert*-butyl carbonium ion via hydride transfer from isobutane, *tert*-butyl carbonium ion with F^- (see model 1-2 in Fig. 1, for which hydrogen fluoride is selected as the catalyst), and *tert*-butyl carbonium ion with isobutene (see model 1-3 in Fig. 1) to describe the addition process of the production of 2,2,4-TMP^+ were focused on. The distance between H14 atom and C15 atom (R_{H14C15}) was defined as the reaction coordinate for model 1-1 and was calculated via the SCAN method with R_{H14C15} reducing. In this way, the potential energy of the system versus R_{H14C15} curve was obtained and a lot of information could be received. Similarly, R_{H7F15} and R_{C1C13} are defined as the scanning coordinates for model 1-2 and model 1-3, respectively. All the models were calculated and optimized using the SCAN method or via the QST3 method (one method of STQN) first, then the transition states (TS's) were found and afterwards validated through frequency analysis. The intrinsic reaction coordinates (IRC) were traced to check the whole reaction path from reactants to products.

Vibrational frequencies were determined firstly to verify the nature of stationary points, secondly to examine zero-point energy corrections on calculating the heat of formation of the molecule, and thirdly to predict vibrational frequencies of the unknown stable species for their future experimental identification by infrared spectroscopy and the assignment of the observed frequencies. The last item is not included in this paper. All the atomic numbers appearing in the context comply with the numbers in Fig. 1. The calculation flowchart is demonstrated in Fig. 2.

3. Results and discussions

3.1. The geometries and properties of ground states

The molecular geometry, charge density and the highest occupied molecular orbital (HOMO) of isobutane are obtained at HF/6-311G** level, as shown in Fig. 3. The framework group is C_{3v}. The positive molecular electrostatic potential is in the middle of the HOMO, which is contributed by the carbon atoms (see Fig. 3). The negative electrostatic potential of the HOMO is mainly contributed by the special hydrogen atom that plays an important role in participating in the following reaction. It is noted that H14 has Lewis acidity prodigiously. This is in close agreement with the charge distribution.



Model 1-1 Model 1-2 Model 1-3

Fig. 1. Three interaction models for calculation. Model 1-1: interaction of protonated 2-butene with isobutane. Model 1-2: deprotonation of *tert*-butyl carbonium ion in the presence of F^-. Model 1-3: interaction of *tert*-butyl carbonium ion with isobutene.

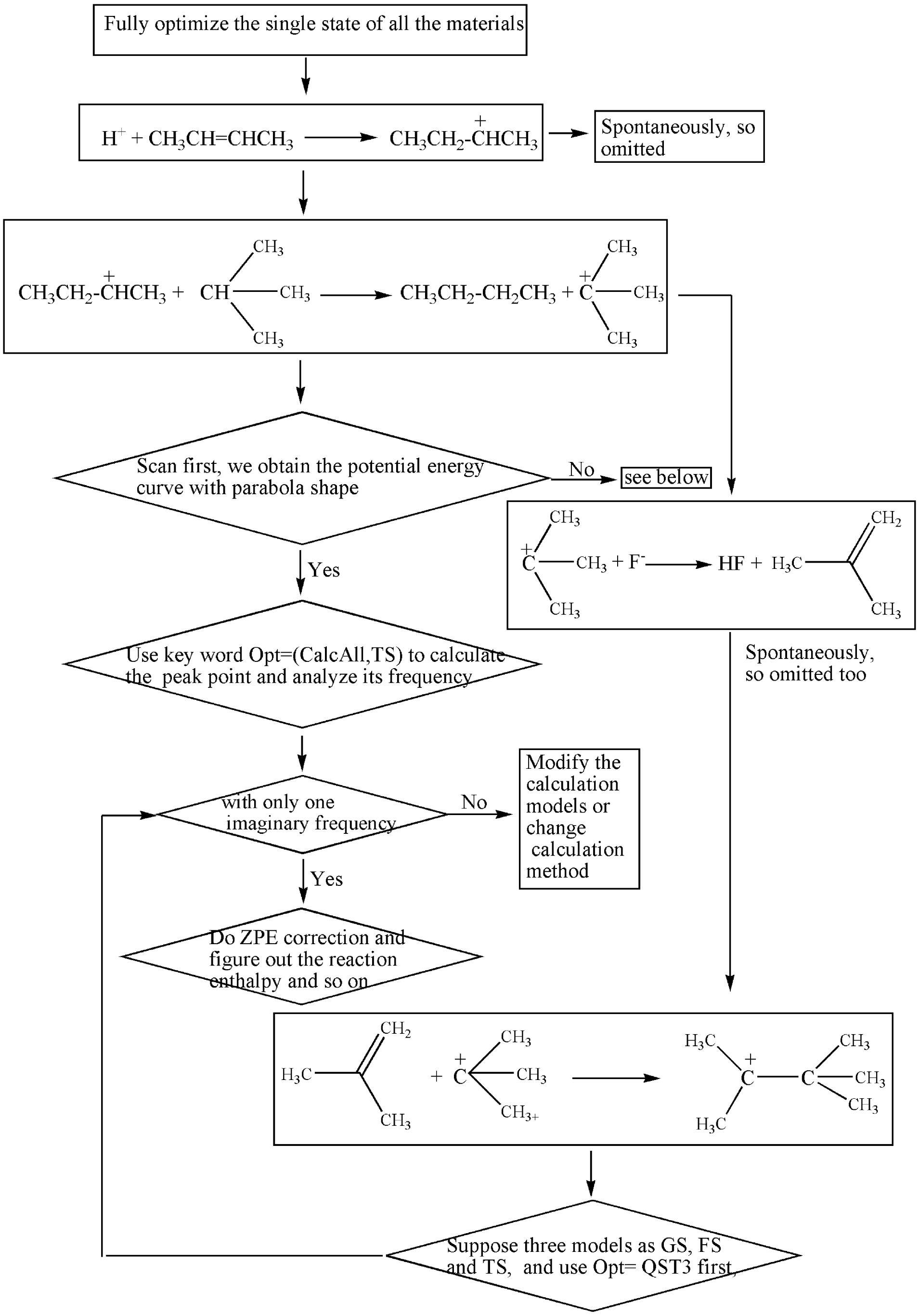


Fig. 2. Calculation flowchart of the reaction steps to be discussed.

The lowest unoccupied molecular orbital (LUMO) of 2-butene and the HOMO of isobutene are demonstrated in Fig. 4. It is evident that the former is contributed by the carbon atoms and the latter is contributed by the double bond of isobutene. So, when they are protonated to form carbonium ions, their activity is originated from the corresponding atoms or groups.

The protonated 2-butene is fully optimized and C16 atom becomes saturated. Upon protonation, the bond length of C15–C16 increases from 0.1318 to 0.1447 nm, while the bond length of C15–C18 slightly decreases to 0.1455 nm. By comparing the changes of charge, it is found that C15 has a positive charge value (0.1560*e*), while other carbon atoms have increased negative charges. These results indicate that C15 is capable of interacting with H14 of isobutane. Now, we can safely say that the models in Fig. 1 are reasonable.

3.2. Interaction mechanism between protonated 2-butene and isobutane

As R_{H14C15} is reduced by 0.01 nm from 0.35 nm, the energy curve of the reaction is obtained at HF/6-311G** level and displayed in Fig. 5. Fig. 5 shows that the energy reaches

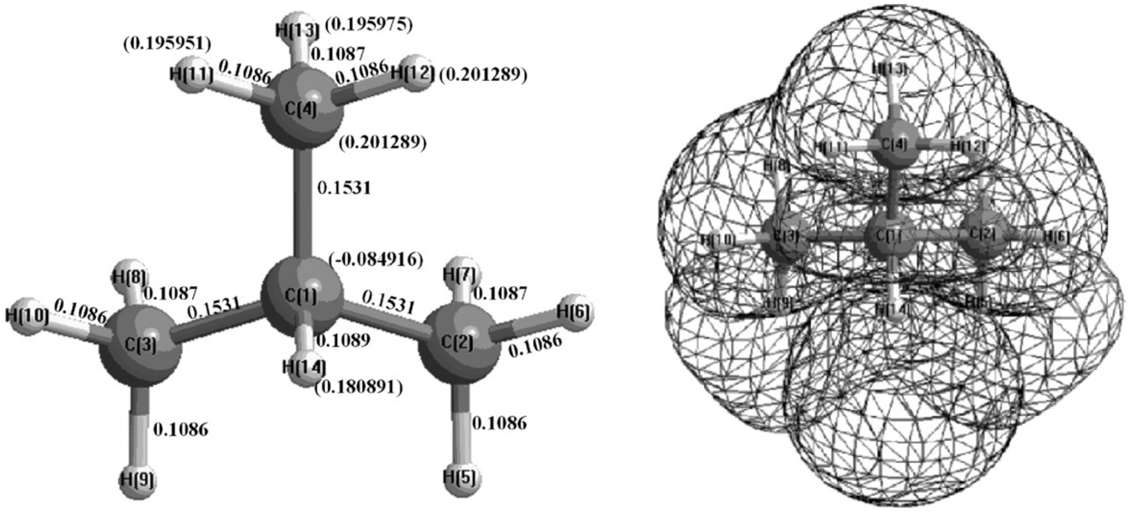
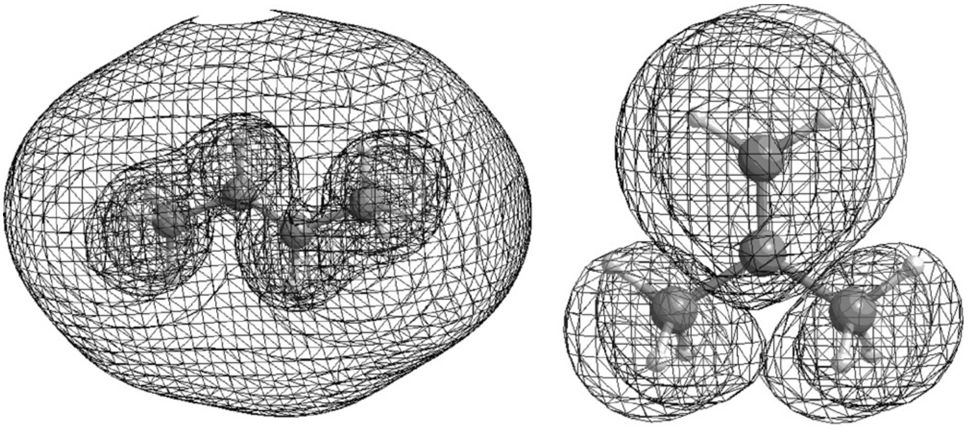


Fig. 3. The geometry and HOMO of isobuane (in nm and *e* in brackets).



LUMO of 2-butene

HOMO of isobutene

Fig. 4. The LUMO of 2-butene and the HOMO of isobutene.

at the highest value at $R_{H14C15} = 0.16$ nm. The energy falls off until H^- is transferred from isobutane to protonated 2-butene. The looking for TS optimization started with the original TS with the highest energy at the highest point of the potential energy curve and only one imaginary frequency $-216.67\ \text{cm}^{-1}$ is calculated from vibration analysis for the TS (Fig. 6a). The result suggests that it is the true TS for the reaction. In the TS structure, angle C15–H14–C1 is 171.61°, signifying that the three atoms are almost in a line. The bond lengths of C15–H14 and C1–H14 are 0.1580 and 0.1165 nm, respectively. In the final state, the H14–C15 bond length is within the normal length range of a traditional C–H bond, while the C1–H14 bond has already been ruptured. The IRC curve (Fig. 7) shows that the reaction proceeds along the coordinate. And the reactants, TS and products are checked too by the beginning point, the peak and the ending point in the curve along the IRC curve, respectively. The TS is the very one mentioned above. Moreover, the calculation result shows that the activation energy of this reaction is 9.36 kJ/mol. This value is very low compared with that of a typical chemical reaction, meaning that this reaction can occur easily. This agrees well with the result of a scaled-up *n*-butene alkylation unit [23].

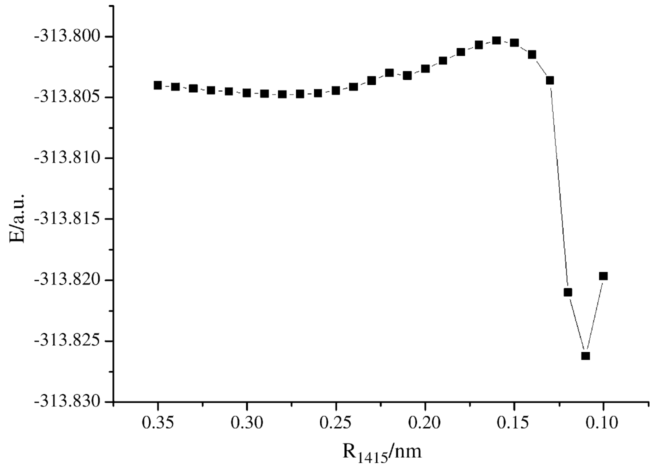


Fig. 5. The potential energy curve of the interaction between protonated 2-butene and isobutane.

A traditional way to calculate enthalpy of a reaction is to calculate heats of formation, and take the appropriate sum and difference. The enthalpy of a reaction with zero-point energy

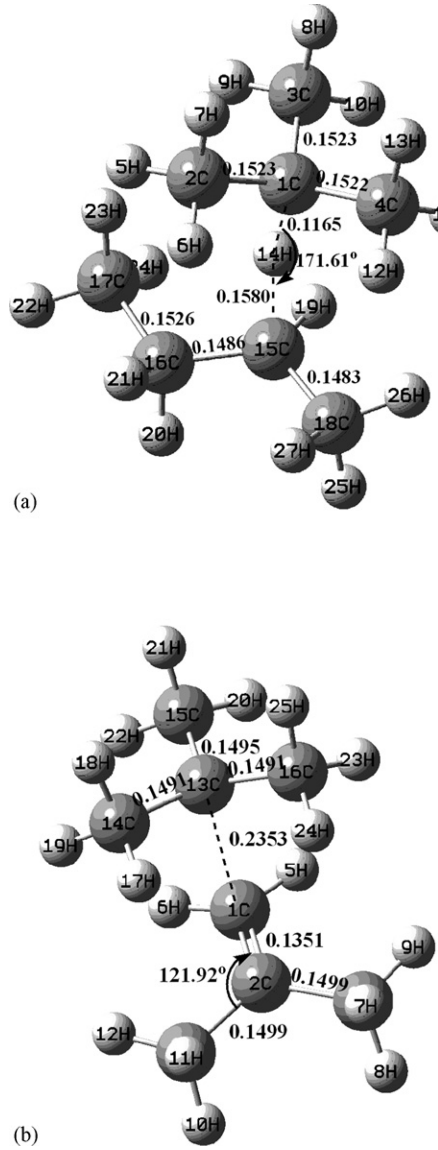


Fig. 6. TS for the interactions (a) between protonated 2-butene and isobutane; imaginary frequency: $-216.67\ \mathrm{cm}^{-1}$ and (b) between *tert*-butyl carbonium ion and isobutene (in nm and degree); imaginary frequency: $-201.03\ \mathrm{cm}^{-1}$.

correction can be calculated simply by [22]:

$$\Delta_{\mathrm{r}}H^{\circ}\,(298\,\mathrm{K}) = \sum_{\text{products}} \Delta_{\mathrm{f}}H^{\circ}\,(298\,\mathrm{K}) - \sum_{\text{reactants}} \Delta_{\mathrm{f}}H^{\circ}\,(298\,\mathrm{K}) \qquad (1)$$

Considering a first order reaction, the reaction rate can be calculated by

$$k(T) = \frac{k_{\mathrm{B}}T}{hc^{0}}\,\mathrm{e}^{-\Delta G^{\circ}_{\mathrm{activ}}/RT} \qquad (2)$$

where k_{B} is Boltzmann constant, $-\Delta G^{\circ}_{\mathrm{activ}}$ is the free energy of activation (the subscript activ denotes activation), h is Plank constant 6.626176×10^{-34} J s, R is ideal gas constant 8.3144 J/(mol K), and $c^{0} = 1$ will be used for the concentration. The calculated results of the enthalpy and the rate (k) of the reaction at 298 K with the zero-point energy correction are -55.89 kJ/mol and $2.2528 \times 10^{3}\ \mathrm{s}^{-1}$, respectively. So it is an exothermic reaction with high reaction rate.

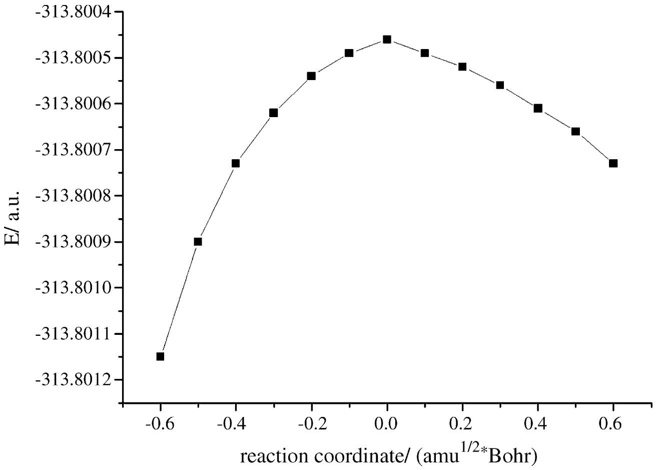


Fig. 7. IRC for the reaction between protonated 2-butene and isobutane.

The tunneling effect of hydride transfer reactions can be estimated. The quantum mechanics tunneling effect correction must be applied to the calculation of the reaction rate constants at lower temperature, where the energy barrier breadth is relatively narrow or quality lepton such as hydrogen atom is dealt with [24]. On the basis of the theories developed by Brillouin, Wentzel, Kramers and Jeffery et al., a JWKB approximation is derived [24], and thereby an equation for calculating trial activation energy is deduced by considering the tunneling effect correction as follows:

$$E_{\mathrm{e}} = E - \left(\frac{N_{\mathrm{A}}}{12}\right)\frac{(h\nu^{\neq})^{2}/(k_{\mathrm{B}}T)}{10^{3}} \qquad (3)$$

where the calculated activation energy (E) 9.36 kJ/mol, Avogadra constant (N_{A}) 6.0221367×10^{23}, imaginary frequency ($\nu^{\neq}$) $-216.67\ \mathrm{cm}^{-1}$, i.e., $-6.5001 \times 10^{12}\ \mathrm{s}^{-1}$, k_{B} 1.380662×10^{-23} J/K, and the temperature (T) 298.15 K are used. The resulting E_{e} is about 9.13 kJ/mol, revealing that the tunneling effect has little influence on this process and thus can be ignored. Whereas, the tunneling effect makes the reaction take place more easily to some degree.

3.3. Deprotonation of tert-butyl cation by interacting with F^{-} to form HF

This reaction can happen spontaneously because of the high reactivity of carbonium ions and the reduced energy of the deprotonated product isobutene. The final state, i.e. hydrofluoric acid and isobutene molecules, calculated at HF/6-311G** level is displayed in Fig. 8. Isobutene would replace 2-butene to react with carbonium ions. Actually, it is one way of enclosing the reaction circle in the form of reducing hydrofluoric acid catalyst.

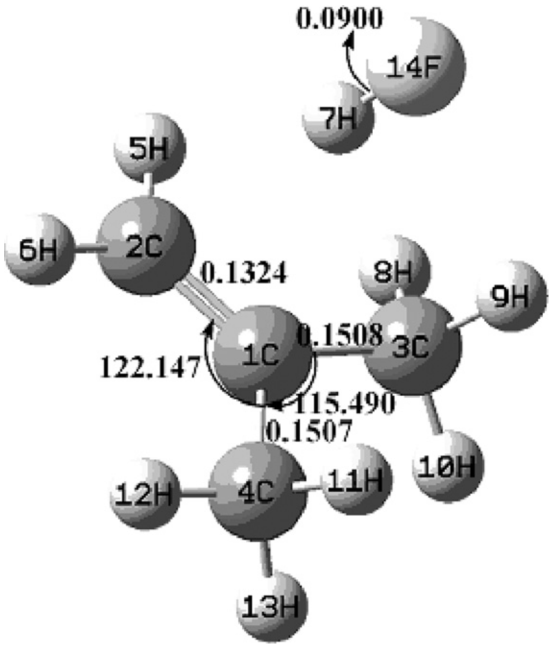


Fig. 8. Final state for the deprotonation of *tert*-butyl carbonium ion and the formation of HF (in nm and degrees).

3.4. Interaction mechanism of tert-butyl carbonium ion and isobutene

The model 1-3 in Fig. 1 is calculated as the beginning state (GS) for the QST3 method and primary TS is obtained with the only imaginary frequency $-201.03\ \mathrm{cm}^{-1}$. Then the key word Opt = TS is used to check the TS structure and the imaginary frequency is verified (Fig. 6b). As R_{C1C13} reduces to 0.1600 nm, the double bond is opened to a single bond of 0.1467 nm, the other bond lengths slightly change correspondingly, and 2,2,4-*tert*-TMP^+ is produced. We can see that the TS obtained before is the real TS for this reaction because it has the highest energy along the reaction coordinate. However, the activation energy for this reaction calculated is −0.0068 a.u. according to its definition, suggesting that the process can happen easily.

In this work, what should be illuminated is that the "TS" does not have the highest energy, but locates at the middle of the potential energy curve, namely the place of the TS and in addition that the "TS" is in the form of typical tertiary carbonium ion. Its nature as intermediate or transition state is confirmed through vibrational analysis, so we still refer it as the transition state. The reaction coordinate for the addition reaction between isobutene and the *tert*-butyl carbonium ion is known to be extremely flat, making it difficult to isolate the true transition state and be thought the normal reaction with energy barrier. The meta-stable intermediate is more appropriate for it. Furthermore, both equilibrium and transition state within the structural convergence criteria used indicate meta-high-frequency imaginary modes unrelated to the reaction chemistry. The anharmonicity of these modes is expected to be large and therefore the calculated harmonic frequency is extremely sensitive to the displacement used in calculating the Hessian. The flat potential energy surface and difficulties in dealing with the vibration modes make isolation and confirmation of transition states through vibrational analysis very tedious and somewhat impractical, requiring large amounts of computational time.

In the same way used for the interaction between protonated 2-butene and isobutane, the enthalpy and the rate (k) of this reaction at 298 K with the zero-point energy correction are −58.02 kJ/mol and $3.0753 \times 10^8\ \mathrm{s}^{-1}$, respectively.

Now the calculation results reveal that the hydride transfer reaction is a key step influencing the alkylation reaction rate and the addition reaction between carbonium ions and butene occurs undemandingly. This is the reason why the isobutane concentration is superfluous higher compared with that of butene in industrial practice.

3.5. Rearrangement of TMP+

An interesting phenomenon is found during the calculation for this reaction. As soon as 2,2,4-*tert*-TMP^+ is formed, the methyl group on isobutene unit rearranges with the scanning, as indicated by the cooperative transformation of the distances of C1–C4 and C2–C4 bonds. Fig. 9 shows that the distances of C1–C4 and C2–C4 bonds change slightly when the two species become closer. When R_{C1C13} approaches to 0.1600 nm, they significantly move to the opposite direction and make the value almost reversed at last, indicating that the methyl group of number 4 carbon is transferred from C1 to C2 atom to form 2,2,3-*sec*-TMP^+. It is probable that this transformation is through a three-member-ring carbonium ion of C1, C2 and C4 as the intermediate. 2,2,3-*sec*-TMP^+ further interacts with isobutane to produce 2,2,3-TMP via a hydride transfer reaction at last.

In addition, 2,3,4-*tert*-TMP^+ formed in C4 alkylation reaction process is also found to rearrange when R_{C1C13} is 0.1400 nm, indicating that the methyl group on isobutyl group is also capable for the rearrangement. The energies of TMP^+ indicate that the sequence of stability is 2,2,4-*sec*-TMP^+ > 2,3,4-*tert*-TMP^+ > 2,2,3-*tert*-TMP^+. In one word,

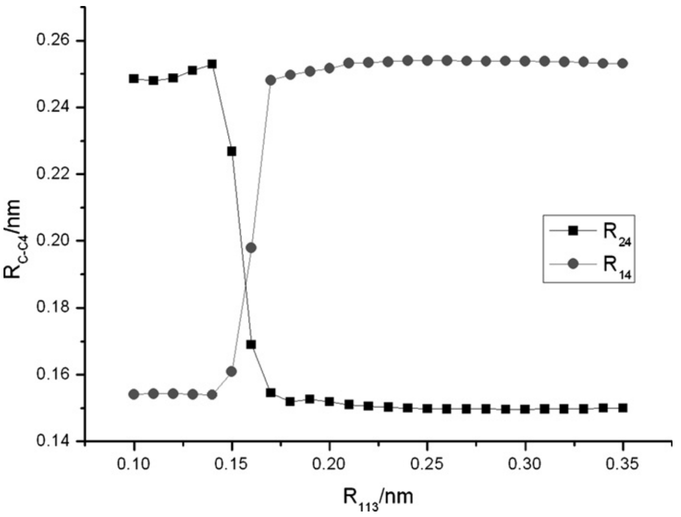


Fig. 9. The description of methyl group transferring during the formation of TMP^+.

the instant reaction for the production of 2,2,3-TMP is dynamically controlled and the production of 2,2,4-TMP is kinetically controlled. The typical product profile from C4 alkylation is 2,2,4-TMP (32.6–48.71%), 2,3,4-TMP (11.8–21.39%) and 2,2,3-TMP (2.4–1.13%) [25,26]. The calculation results are satisfactorily consistent with the experimental data and perfectly explain the diversity of product profiles in industrial practice.

4. Conclusions

The TS for hydride transfer from isobutane to protonated 2-butene is obtained. $-216.67\ \mathrm{cm}^{-1}$ is the only imaginary frequency. The activation energy calculated is very low (9.13 kJ/mol with tunnelling effect correction). Once the *tert*-butyl carbonium ion is formed via hydride transfer from isobutane to protonated 2-butene, the reaction occurs ceaselessly.

Both the potential energy curve and the TS structure are obtained from the calculation of the interaction of *tert*-butyl cation with isobutene. The TS has only one imaginary frequency, i.e. $-201.03\ \mathrm{cm}^{-1}$. The calculated activation energy is below zero. The produced TMP carbonium ion can rearrange its structure to form various species through a cyclic carbonium ion intermediate. Based on this viewpoint, the variety of products observed in practice can be well explained.

The two reactions, the hydride transfer reaction from isobutane and the addition reaction between *tert*-butyl carbonium ion and butene occur easily under strong acid circumstances, which is consistent with the experimental results. In the instant reaction the production of 2,2,3-TMP is kinetically controlled, the production of 2,2,4-TMP is thermodynamically controlled.

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