Catal Lett (2012) 142:287–293
DOI 10.1007/s10562-011-0755-3

Theoretical Studies of Species Related to Acrolein Hydrogenation

Guo-Jun Kang · Jing Ma · Zhao-Xu Chen

Received: 20 August 2011 / Accepted: 2 December 2011 / Published online: 20 December 2011

Abstract Unsaturated alcohols, usually produced from selective hydrogenation of unsaturated aldehydes, are important fine chemical intermediates used to synthesize pharmaceuticals and flavoring materials. Acrolein, the smallest member in α, β-unsaturated aldehydes, is the model system for studying selective hydrogenation of α, β-unsaturated aldehydes. So far most theoretical work is about adsorption and reactions of acrolein and its related species on surfaces. In the present paper we systematically studied the geometries, electronic structures, stability and transformation of various species derived from stepwise hydrogenation of acrolein in the gas phases. We identified the most stable intermediates for each system and determined the energy barrier for intermolecular conversion between isomers for various species with different content of hydrogen. All these results are valuable and informative for understanding the surface chemistry of hydrogenation of α, β-unsaturated aldehydes.

Keywords Gas-phase kinetics · Reaction intermediates · Isomerization · Hydrogenation

1 Introduction

Allyl alcohols are important fine chemical intermediates for synthesizing pharmaceuticals and flavoring materials [1, 2]. Selective hydrogenation of α, β-unsaturated aldehydes is a useful means to produce allyl alcohols. Thermodynamically the C=C bond is more active than the C=O bond [3, 4]. Recently Claus et al. [4–6]. found that the conventionally catalytically inert gold exhibits unexpected activity for the selective hydrogenation of α, β-unsaturated aldehydes to allyl alcohols, which re-initiates interests on hydrogenation of α, β-unsaturated aldehydes [6–12]. Acrolein (CH_2=CH–CH=O) is the first member of α, β-unsaturated aldehyde and its selective hydrogenation to allyl alcohol is most difficult because there are no substitution groups on the carbon atoms of the C=C bond. For this reason it is often used as a model system for studying selective hydrogenation of α, β-unsaturated aldehyde both experimentally and theoretically [6, 8]. As far as we know, theoretical studies mainly devoted to adsorption and reactions of acrolein and various hydrogenated species on metal or alloy surface [8, 10–12], and less attention is paid to the molecular structures, stability and transformation of the species derived from acrolein hydrogenation.

Theoretically there are various hydrogenation products. If two H atoms are added, six types of species: 3210, 3111, 2121, 2211, 3120 and 2220 can be formed (we use *klmn* to denote these species. Here *k, l, m* and *n* are integers which represent the number of H atom bonding to C1, C2, C3 and O atoms of acrolein, respectively. The atom numbering of acrolein is C1–C2–C3–O. For example, 3210 means that there are three, two and one H atoms bonded to C1, C2 and C3 atoms, respectively, and the O atom has no H atom.). Experimentally only 3210 and 2121 which account for more than 90% of the partial hydrogenation products are produced

Electronic supplementary material The online version of this article (doi:10.1007/s10562-011-0755-3) contains supplementary material, which is available to authorized users.

G.-J. Kang · J. Ma · Z.-X. Chen (✉)
Key Laboratory of Mesoscopic Chemistry of MOE,
Institute of Theoretical and Computational Chemistry,
School of Chemistry and Chemical Engineering, Nanjing
University, Nanjing 210093, People's Republic of China
e-mail: zxchen@nju.edu.cn

G.-J. Kang
Low Carbon Energy Institute, China University of Mining
and Technology, Xuzhou 221008, People's Republic of China

preferentially on catalysts, and the complete hydrogenation products are rather few [6, 13]. Then questions arise, why other products such as 3111, 2211, 3120 and 2220 are rare? Is this due to isomerization of these species to 3210 or 2121 after they desorb from the surface into the gas phase or due to other factors such as the stability and formation barriers of them on surfaces? Obviously the answers to these questions are meaningful for a comprehensive understanding of the surface chemistry of acrolein on metal surfaces and for improving the hydrogenation selectivity to allyl alcohols. With this in mind, we recently carried out a density functional study of various species originated from acrolein stepwise hydrogenation. Apart from the geometries of the species, we investigated their stability and the likelihood of the transformation between isomers.

2 Computational Methods

We used generalized gradient approximation (GGA)-PW91 functional [14, 15] with medium size 6-31G(d, p) basis sets implemented in Gaussian 03 program package [16]. Larger basis sets of 6-311G(d, p) did not alter the ordering of the relative stability and only negligibly affect the structures. All the located structures are verified to be local minima on potential energy surfaces. Transition states of isomerization were located and were further confirmed with intrinsic reaction coordinate (IRC) method to ensure that they connect the right reactants and products.

3 Results and Discussion

Figure 1 shows all the species derived from stepwise hydrogenation of acrolein. These species, according to the number of H atom, can be classified into five classes: the 4H (meaning the species containing four H atoms), the 5H, the 6H, the 7H and the 8H systems. With our *klmn* notation, the 4H system (acrolein) is denoted as 2110. The 5H system contains four species 3110, 2210, 2120, and 2111; the 6H system is composed of six species 3210, 3120, 3111, 2220, 2211 and 2121; there are four types of species in the 7H system: 3220, 3211, 3121 and 2221, and finally the 8H system possesses only one species 3221 which is the fully hydrogenated product of acrolein. Usually each species may have *cis*- and *trans*-configurations. Unless stated explicitly we present and discuss the most stable configuration.

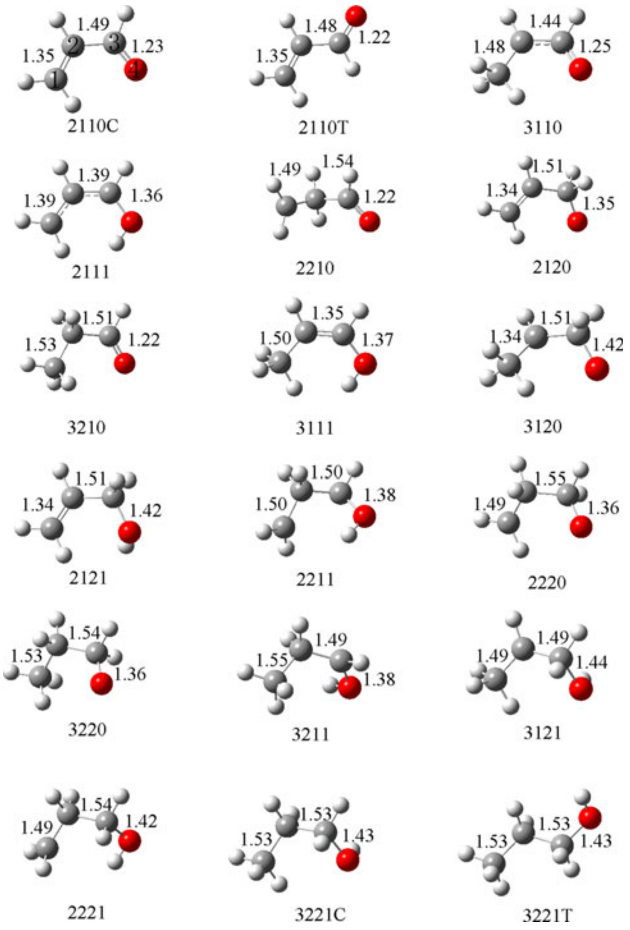

Fig. 1 Geometrical parameters (unit: Å) of species relevant to acrolein hydrogenation at the PW91PW91/6-31G** level

3.1 The 4H System

Acrolein (2110) may exist in the *cis*- and *trans*-forms. The *trans*-isomer is 7 kJ/mol more stable than the *cis*-isomer (Table 1), in agreement with the previous theoretical result [17] and the experimental observation that 96% of the molecules adopt the *trans*-form in the gas phase at room temperature [18]. The ratio of the *cis*-isomer to *trans*-isomer increases with the increase of temperature. At 600 K *cis*-isomer reaches $\sim$40% in the equilibrium mixture of *cis*- and *trans*-acrolein. Our calculated transformation barrier from *cis*-acrolein to *trans*-acrolein is 30 kJ/mol, indicating that inter-conversion between *cis*- and *trans*-acrolein is facile even at room temperature. This result implies that both *cis*- and *trans*-isomers can be present under hydrogenation condition.

The C1–C2 bond of acrolein, 1.35 Å (Fig. 1), features a typical C=C bond; the C2–C3 bond length of $\sim$1.49 Å is between the single and double C–C bond lengths, due to conjugation effect. It is noted that the C2–C3 and C3–O bonds in the *cis*-isomer (2110C) is 0.01 Å longer than that in the *trans*-counterpart (2110T). The calculated Mulliken atomic charges on C1, C2, C3 and O are $-0.245e$, $-0.069e$, $0.240e$, $-0.382e$ for *trans*-acrolein and $-0.216e$, $-0.098e$, $0.232e$, $-0.377e$ for *cis–trans*, respectively (Table 2). These results show that most electrons are

Table 1 Relative stability (in kJ/mol) of various species relevant to acrolein hydrogenation at PW91PW91/6-31G** level

4H		**5H**		**6H**		**7H**	
4TS	30	5TS$_{13}$	170	6TS$_{13}$	332	7TS$_{12}$	146
2110C	0	5TS$_{24}$	116	6TS$_{DH}$	235	7TS$_{23}$	137
2110T	−7	5TS$_{14}$	−17	6TS$_{24}$	182	7TS$_{13}$	128
		5TS$_{34}$	82	2220	260	7TS$_{34}$	101
		5TS$_{23}$	45	3120	245	7TS$_{24}$	87
8H		5TS$_{12}$	25	2211	229	7TS$_{14}$	59
8TS	15	2120	0	2121	0	2221	0
3221T	0	2210	−72	3111	−37	3220	−8
3221C	−1	2111	−99	3210	−82	3121	−17
		3110	−133			3211	−33

klmn denotes the number of H atom(s) bonding to C1,C2,C3 and O atoms, respectively. *NTS*$_{mn}$ represents the transition state of H-shift between the *n*th and *m*th atom, *N* is the number of total hydrogen atom in the system

Table 2 Mulliken atomic charges and Mulliken atomic spin density of various isomers relevant to acrolein hydrogenation at PW91PW91/6-31G** level

	Mulliken atomic charges (*e*)				Mulliken atomic spin density (*e*)			
	C1	C2	C3	O4	C1	C2	C3	O4
2110C	−0.216	−0.098	0.232	−0.377	–	–	–	–
2110T	−0.245	−0.069	0.240	−0.382	–	–	–	–
2120	−0.239	−0.073	−0.022	−0.322	0.064	−0.024	−0.041	0.800
2210	−0.237	−0.301	0.257	−0.357	1.076	−0.070	0.012	0.001
2111	−0.309	−0.064	0.082	−0.449	0.633	−0.158	0.508	0.100
3110	−0.409	−0.065	0.214	−0.388	−0.049	0.762	−0.062	0.318
2220	−0.243	−0.242	−0.004	−0.301	1.067	−0.062	−0.023	0.839
3120	−0.397	−0.083	−0.021	−0.297	−0.073	1.009	−0.081	0.879
2211	−0.269	−0.265	0.066	−0.449	1.045	−0.106	0.867	0.157
2121	−0.262	−0.076	−0.022	−0.502	–	–	–	–
3111	−0.406	−0.116	0.104	−0.473	–	–	–	–
3210	−0.358	−0.291	0.261	−0.361	–	–	–	–
2221	−0.263	−0.245	0.010	−0.504	1.047	−0.068	0.030	0.008
3220	−0.364	−0.228	0.002	−0.306	0.002	0.005	−0.037	0.840
3121	−0.389	−0.114	−0.014	−0.502	−0.069	0.982	−0.052	0.023
3211	−0.349	−0.275	0.072	−0.451	0.050	−0.042	0.864	0.138
3221T	−0.369	−0.233	0.014	−0.510	–	–	–	–
3221C	−0.353	−0.234	0.005	−0.502	–	–	–	–

accumulated on the terminal C1 and terminal O atoms. In fact, the terminal C1 and O atoms of most species studied in the present paper possess most negative charges, indicating that electrophilic reagents would attack these positions favorably when reactions are charge controlled.

3.2 The 5H System

Hydrogen atom may attack at four sites of acrolein, which results in four radicals: 3110, 2111, 2210 and 2120 [19]. According to our recent work on Au(110) [9] and Au$_{20}$ [11], radicals bind to substrates via atoms with an unpaired electron favorably.

The most stable isomer is 3110 (Table 1). Unlike acrolein where the *trans*-isomer is 7 kJ/mol more stable than the *cis*-one, the *cis*-3110 turns out to be 3 kJ/mol more stable than the *trans*-isomer. In fact, all the *cis*-isomers in the 5H system are more stable than the corresponding *trans*-isomers. Compared with acrolein, the C1–C2 distance is elongated by 0.13 to 1.48 Å (Fig. 1), slightly shorter than the single C–C bond length of 1.53 Å in ethane at the same computational level of PW91PW91/6-31G**. The C2–C3 bond is reduced by about 0.05 Å compared to that in acrolein. Variation of the C3–O bond length is very small, ~0.02 Å, with respect to that in acrolein. 2111 is the next stable isomer derived from hydrogen addition at the terminal oxygen of acrolein. It is 34 kJ/mol less stable than 3110, indicating that the first hydrogenation at C1 is thermodynamically more favorable than that at O. 2111 has two equal C–C bonds, 1.39 Å, indicative of the significant conjugation effect. The C3–O, 1.36 Å, is longer than 1.25 Å in 3110 (Fig. 1). 2210 is 61 kJ/mol higher in energy than 3110. The C1–C2 length is close to that in 3110 and is between a single and a double C–C bond. The C2–C3 distance of 1.54 Å shows that this bond is essentially a single C–C bond. The C=O, 1.22 Å, is the shortest among the four species in the 5H system. Hydrogen atom attacking at C3 of acrolein produces 2120 species. As can be seen from Table 1, 2120 is the least stable species in the 5H group, implying that hydrogen attacking at C3 is thermodynamically most unlikely, compared with the other three sites. The calculated C1–C2 and C2–C3 bond lengths, 1.34 and 1.51 Å, respectively, clearly show that they are double and single bonds, respectively.

Mulliken atomic charges are −0.409*e* (C1), −0.065*e* (C2), 0.214*e* (C3), −0.388*e* (O) for 3110 species (Table 2), meaning that most electrons are distributed on the terminal C1 and O atoms. The calculated Mulliken atomic spin density is −0.049*e* (C1), 0.762*e* (C2), −0.062*e* (C3), 0.318*e* (O). Previous calculations [9, 11, 12, 20] indicate that the interaction of acrolein and its derived species with metal surfaces is orbital controlled, rather than charge controlled. Thus, the atoms with most negative charges are not the atoms dominating the interaction with catalyst surfaces. Analyses of the electronic structure of 3110 reveal that density of electrons of the frontier molecular orbitals (MOs) is mostly on C2 and O that have high spin density. According to the frontier molecular orbital theory [21], adsorption of 3110 will take place favorably through C2 and O, which is supported by our test calculation of 3110 adsorption on Au_4 cluster. In fact, for the radicals studied here (see species with net spin density in Table 2) the density of electrons of the frontier MOs is also largely distributed on the atoms with higher spin density. Hence these open-shell species are expected to interact with metal surfaces through these atoms, in agreement with our results [22]. The calculated Mulliken charges of 2111 are −0.309*e* (C1), −0.064*e* (C2), 0.082*e* (C3) and −0.449*e* (O), and the spin density, C3 (0.508*e*) and C1 (0.633*e*), indicates that the unpaired electron is distributed on these two atoms through which this species interacts favorably with the substrate, in accordance with our recent calculations [12]. C1, C2, C3 and O are charged with −0.237*e*, −0.301*e*, 0.257*e* and −0.357*e*, respectively in 2210. The spin densities on C1 are the largest (1.076*e*), meaning that C1 will dominate the adsorption of 2210. The terminal C1 and O atoms are most negatively charged, −0.239*e* and −0.322*e*, respectively in 2120. The unpaired electron is mainly located on the O as indicated by the calculated spin density (0.800*e*).

It is believed that acrolein hydrogenation follows a stepwise hydrogenation mechanism and the group via which the species interacts with catalysts will be preferentially hydrogenated [4]. As mentioned above, 2121 (allyl alcohols) are the desired product of acrolein hydrogenation. Assuming that unpaired electrons dominate the adsorption of a species, one would expect that 2120 is more favorable for production of allyl alcohols than 2111 because the unpaired electron in the former is on the O atom while in the latter the unpaired electron is located on C1 and C3 (Table 2).

Above we show that 3110 is the most stable species in the 5H group. Now we discuss the kinetic feasibility of transformation from the less stable species (2111, 2210 and 2120) to 3110 via H-shift. Figure 2 displays the potential energy surfaces (PES). There are three one-step or direct H-shift pathways: (i) 2120 → 3110, (ii) 2210 → 3110 and (iii) 2111 → 3110. The calculated barriers are 170(i), 97(ii) and 82(iii) kJ/mol, respectively, which implies that the most favorable pathway is 2111 → 3110(iii). At hydrogenation reaction temperatures (500 K) such transformation in the gas phase is likely to happen (using an exponential factor of 10^{13}, we estimate a rate constant $k = 2.71 \times 10^4\ s^{-1}$). The conversion of 2210 to 3110 needs to overcome a slightly high barrier, 97 kJ/mol. This reaction is also likely to occur. Direct transformation of 2120 to 3110 is difficult with a barrier as high as 170 kJ/mol. However, 2120 may convert to 3110 via a two-step process (2120 → 2111 → 3110). This process has two equal barriers (82 kJ/mol). Therefore, 2120 may convert to 3110. To sum up, under the hydrogenation condition, conversion

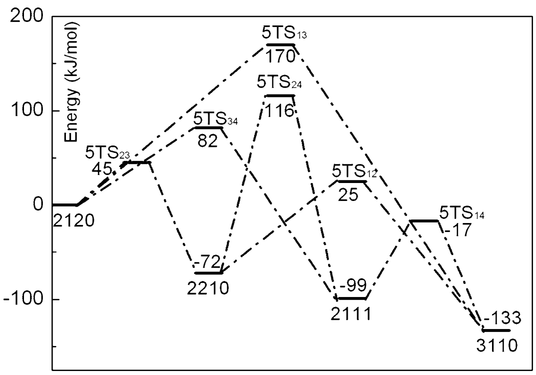

Fig. 2 Energy profiles of acrolein hydrogenation in the 5H group. The energy zero point refers to the energy of 2120

of less stable species 2111, 2210 and 2120 to most stable 3110 can be expected. With 2111 and 2210 the direct conversion is kinetically the most favorable routes whereas a two-step pathway is more favorable for transformation of 2120–3110. One thing has to be pointed out. The above discussion refers to gas phase. For the 5H systems, because they bind strongly with catalysts, desorption from the surface into gas phase is hard. On catalyst surfaces, transformation barriers will be different from the results in the gas phase.

3.3 The 6H System

The 6H system contains six species: 3210, 2121, 3111, 3120, 2211 and 2220. These species can be divided into two categories according to their electronic states: singlet state species including 3210, 2121 and 3111, and triplet species having 3120, 2211 and 2220. The latter are diradicals. The stability of the *trans*-isomers of 2220 and 3111 is higher or equal to that of the *cis*-isomers. For the rest four species of the 6H system the *cis*-isomers are more stable than the corresponding *trans*-isomers.

Partial hydrogenation of acrolein favorably produces propionaldehyde (3210) on supported Pt, Rh and Pd catalysts [4, 16]. Our calculations show that 3210 is the most stable among the six 6H species (Table 1) in the gas phase. In this species, the two C–C bonds are 1.51 and 1.53 Å, close or equal to the C–C single bond length of 1.53 Å of ethane. On the other hand, the C=O bond is 0.01 Å shorter than 1.23 Å in 2110C, indicating that this bond tends to be stronger when the C1=C2 bond is saturated. The next stable species is 3111 (Table 1), 45 kJ/mol less stable than 3210. The C2–C3 bond, 0.14 Å shorter than that in acrolein (1.49 Å), is a double bond. The C3–O distance, 1.37 Å, is between 1.23 (2110C) and 1.43 Å (3221C), implying that C3–O possesses some characteristics of a double bond. Hydrogenation of the C=O bond of acrolein leads to 2121 or allyl alcohol (AyOH), the desired products of selective hydrogenation of α, β unsaturated aldehyde [3]. Its C=O bond changes from 1.23 Å in acrolein to 1.42 Å in 2121. Thermodynamically, 2121 is 82 kJ/mol less stable than 3210 and 37 kJ/mol less stable than 3111.

As pointed out in the introduction, 2121 is the valuable intermediate used to synthesize pharmaceuticals and flavoring materials and selective production of it from hydrogenation of α, β-unsaturated aldehydes attracts attention [1, 2], and the yields of 3210 and 2121 account for more than 90% of the hydrogenated products. However, 3111, though more stable than 2121 in gas phase, is rarely produced on catalysts. 3210 can be formed from hydrogenation of 2210 and 3110; 2121 can be produced from H addition of 2120 and 2111 while 3111 can be obtained from hydrogenation of 2111 and 3110. The least yield of 3111 may be due to either less 2111 and 3110 on the surface or unfavorable conversion kinetics from 2111 and 3110 to 3111. Since 2111 and 3110 can easily convert into 2121 and 3210, the low quantity of 3111 should be owing to the unfavorable surface kinetics from 2111 and 3110 to 3111, unless 2111 and 3110 is difficult to produce.

Figure 3 shows that PES for the isomerisation among the three singlet 6H species. Transformation of 3111 to 3210 needs to overcome a barrier of 219 kJ/mol. Direct conversion of the least stable 2121 to 3210 is computed to have a barrier of 235 kJ/mol. The barrier for the conversion of 2121 to 3111 is the highest, 332 kJ/mol. Therefore, transformation among the three isomers is difficult. This result implies that the hydrogenation yield of 2121 (allyl alcohol) is determined by its formation on catalyst surfaces and one need not worry about the transformation of the desired 2121 to the undesired 3210 in the gas phase. In addition, our results further show that the low yield of 3111 is due to the surface chemistry of these species on catalysts, not the transformation to 3210.

The most stable triplet species in the 6H system is 2211 which is 311 kJ/mol less stable than 3210 (Table 1). The two C–C bond lengths are equal, 1.50 Å, and the C3–O distance, 1.38 Å, is similar to that in 3111. 3120 is 16 kJ/mol less stable than 2211. The C2–C3 (1.51 Å) and C3–O (1.42 Å) bonds are single C–C and C–O bonds in 3120. The C1–C2 bond, 1.34 Å, indicates that it is a double bond. The least stable triplet 6H species is 2220 which is 15 kJ/mol higher in energy than 3120. All the three triplet species are diradicals, as evidenced by the calculated spin density (Table 2). For example, the spin densities for 3120 are 1.009*e*(C2) and 0.879*e*(O), indicating that the unpaired electrons are mainly located on C2 and O. Since these triplet species possess unpaired electrons, they are expected to interact favorably with metal substrates, though triplet species are more than 310 kJ/mol unstable than the singlet species in the gas phase (Table 1). In addition, transformation among the three triplet species is relatively easy with the barrier of less than 100 kJ/mol (not shown).

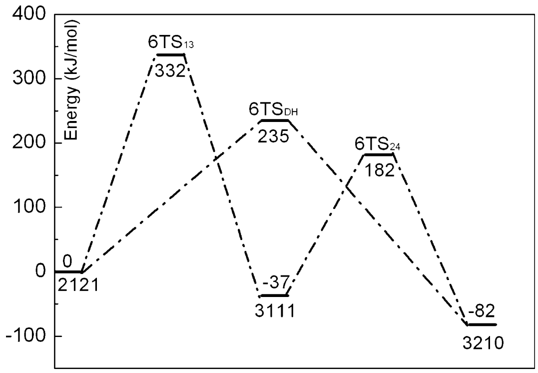

Fig. 3 Energy profiles of acrolein hydrogenation in the 6H group

3.4 The 7H System

Addition of three H atoms to acrolein produces four radicals: 3211, 3121, 2221 and 3220. The *cis*-isomers of 2221 and 3121 are more stable than the respective *trans*-isomers whereas the *trans*-isomers of 3220 and 3211 are lower in energy than the *cis*-isomers. The ordering of stability is 3211 > 3121 > 3220 > 2221. The C1–C2 and C2–C3 bonds in the most stable 3211 which is 33 kJ/mol lower in energy than 2221, are basically single bonds, being 1.55 and 1.49 Å, respectively. The C3–O bond length, 1.38 Å, is between the single and double bond distances (Fig. 1). C1, C2 and O atoms are negatively charged and C3 is practically neutral (0.072*e*). The calculated Mulliken atomic spin density indicates that the unpaired electron is mainly distributed on C3 (0.864*e*). Therefore, C3 is the "active atom" that contributes the most to the interactions of 3211 with metal substrates. The next stable isomer 3121 is 17 kJ/mol more stable than 2221. Here the active atom is C2 with a spin density of 0.982*e* (Table 2). The charges on C1, C2, C3 and O atoms are −0.389*e*, −0.114*e*, −0.014*e* and −0.502*e*, respectively. The C1–C2 and C2–C3 lengths are the same, 1.49 Å, which is slightly shorter than the single C–C bond length of 1.53 Å in ethane. The C–O bond is 1.44 Å. 3220 is 8 kJ/mol more favorable than 2221 (Table 1). The unpaired electron is located on the O with the spin density of 0.840*e*. The C1–C2 and C2–C3 lengths, 1.53 and 1.54 Å, respectively, are close to the single C–C bond in ethane (1.53 Å) while the C–O bond is 1.36 Å. The most unstable isomer in this group is 2221. The C1–C2 and C2–C3 are 1.49 and 1.54 Å, showing that the latter possesses more single C–C bond characteristics. The C3–O bond is 1.42 Å long. The calculated spin densities of 1.047*e* on C1 (Table 2) indicate that C1 will interact the most strongly with the substrate.

Figure 4 displays the PES for transformation among the four species in the 7H system. As can be seen from Fig. 4, the lowest barrier for the direct conversion to the most stable 3211 is calculated to be 109 kJ/mol from 3220 to 3211. The next is 2221 to 3211, 128 kJ/mol, followed by 154 kJ/mol from 3121 to 3211. Inter-conversion between the three less stable species seems kinetically more favorable, compared to their transformation to 3211. The most facile process is from 2221 to 3220 with a barrier of 59 kJ/mol. Direct conversion of 2221 to 3121 needs to cross a barrier of 146 kJ/mol. Note the barrier from 3220 to 3121 is 95 kJ/mol. Thus, transformation of 2221 to 3121 can relatively easily proceed via an indirect conversion, first to 3220 and then to 3121.

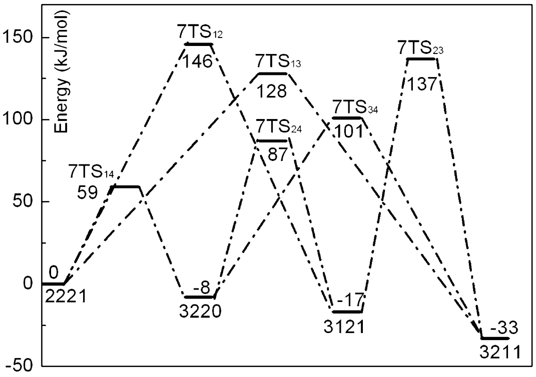

Fig. 4 Energy profiles of acrolein hydrogenation in the 7H group

3.5 The 8H System

Complete hydrogenation of acrolein produces 3221 (propanol). It has two tautomers (*trans*-isomer 3221T and *cis*-isomer 3221C) due to the rotation of the hydroxyl group around the C–O bond axis. The energy difference between the two tautomers is negligible (3221C is only 1 kJ/mol more stable than 3221T). The energy barrier is about 15 kJ/mol from the *trans*-isomer to the *cis*-one. Such a low barrier and essentially equal stability indicate that 3221T and 3221C can coexist in the gas phase at room temperature with almost equal concentration. The C–C bond lengths of 1.53 Å is equal to the single C–C bond distance in ethane and the C3–O bond, 1.43 Å, is a single bond. C1, C2 and O are negatively charged (−0.353*e*, −0.234*e* and −0.502*e*, respectively) while C3 is almost neutral (0.005*e*).

4 Conclusions

We have performed density functional studies of species relevant to acrolein hydrogenation. We identified the most stable species in each group. Thermodynamically the most favorable route of complete hydrogenation of acrolein is 2110T → 3110 → 3210 → 3211 → 3221C in the gas phase. Furthermore, we examined the transformation between isomers among each group and found that transformation barrier ranges from 45 to 332 kJ/mol. Our calculations demonstrate that the triplet radicals in the 6H system are much high in energy, rationalizing the very low yields of these species on catalysts. The undesired aldehyde 3210 is more stable than 2121 in the gas phase. According to the present calculations, the selective production of allyl alcohols must be due to surface chemistry rather than gas phase chemistry. One needs not worry about the transformation of the hydrogenated 6H species in the gas phases, and the very low production of 3111 is due to the surface chemistry of hydrogenation reactions.

Acknowledgments Financial supports from NSFC No. 20573052 and 20973090, 973 Program 2009CB623504 and 2011CB808604 are acknowledged.

References

1. Gallezot P, Richard D (1998) Catal Rev Sci Eng 40:81
2. Marinelli TBLW, Nabuurs S, Ponec V (1995) J Catal 151:431
3. Mohr C, Hofmeister H, Radnik J, Claus P (2003) J Am Chem Soc 125:1905
4. Claus P (1998) Top Catal 5:51
5. Claus P, Hofmeister H, Mohr C (2004) Gold Bull 37:181
6. Claus P (2005) Appl Catal A 291:222
7. Lim KH, Chen ZX, Neyman KM, Rosch N (2006) Chem Phys Lett 420:60
8. Loffreda D, Delbecq F, Vigne F, Sautet P (2006) J Am Chem Soc 128:1316
9. He X, Chen ZX, Kang GJ (2009) J Phys Chem C 113:12325
10. Lim KH, Mohammad AB, Yudanov IV, Neyman KM, Bron M, Claus P, Rösch N (2009) J Phys Chem C 113:13231
11. Li Z, Chen ZX, He X, Kang GJ (2010) J Chem Phys 132:184702
12. Kang GJ, Chen ZX, Li Z (2011) Catal Lett 141:996
13. Mohr C, Hofmeister N, Lucas M, Claus P (2000) Chem Eng Technol 23:324
14. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1992) Phys Rev B 46:6671
15. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C (1993) Phys Rev B 48:4978(E)
16. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA (2004) Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford
17. Delbecq F, Sautet P (2002) J Catal 211:398
18. Blom CE, Grassi G, Bauder A (1984) J Am Chem Soc 106:7427
19. FitzPatrick BL, Lau KC, Butler LJ, Lee SH, Lin JJM (2008) J Chem Phys 129
20. Delbecq F, Sautet P (2002) J Catal 211:39
21. Jensen F (2007) Introduction to computational chemistry. Wiley, New York
22. Li Z, Ding WP, Kang GJ, Chen ZX (2012) Catal Commun 17:164