

STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Quantum-Chemical Simulation of the Allyl Isomerization of Allylbenzene in the Presence of Gold Atom

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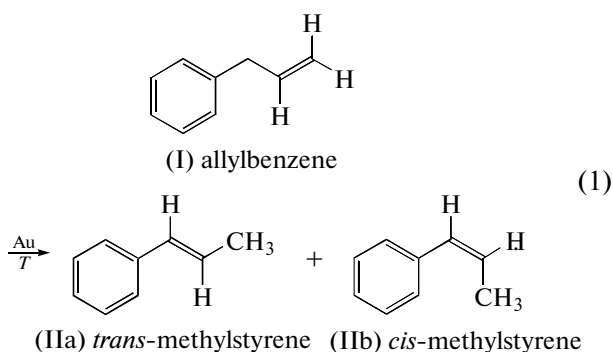
Abstract—The isomerization of allylbenzene into *trans*- and *cis*- β -methylstyrene was simulated by the PBE density functional method for the allylbenzene–Au^z ($z = 0, +1$) system. It was discovered that the activation energy falls and the rate constant of allylic isomerization of allylbenzene rises upon the transition from Au⁰ to Au⁺. The experimentally observed preferential formation of *trans*-isomer is verified by our calculations.

Keywords: Allylbenzene, density functional method, double bond isomerization, gold.

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INTRODUCTIONS

Gold nanoparticles (NPs) exhibit high activity in oxidation, hydrogenation, the conversion of water vapor, and hydrodechlorination [1–4]. Until recently, only mechanisms of redox reactions with nanosized gold had been studied in detail; it was discovered that the most active catalytic centers are the cationic form of gold Au ^{δ +} ($0 < \delta < 1$) [4]. As was recently shown in [5, 6], immobilized gold NPs are effective catalysts of the double bond migration (allylic isomerization) in allylbenzene:



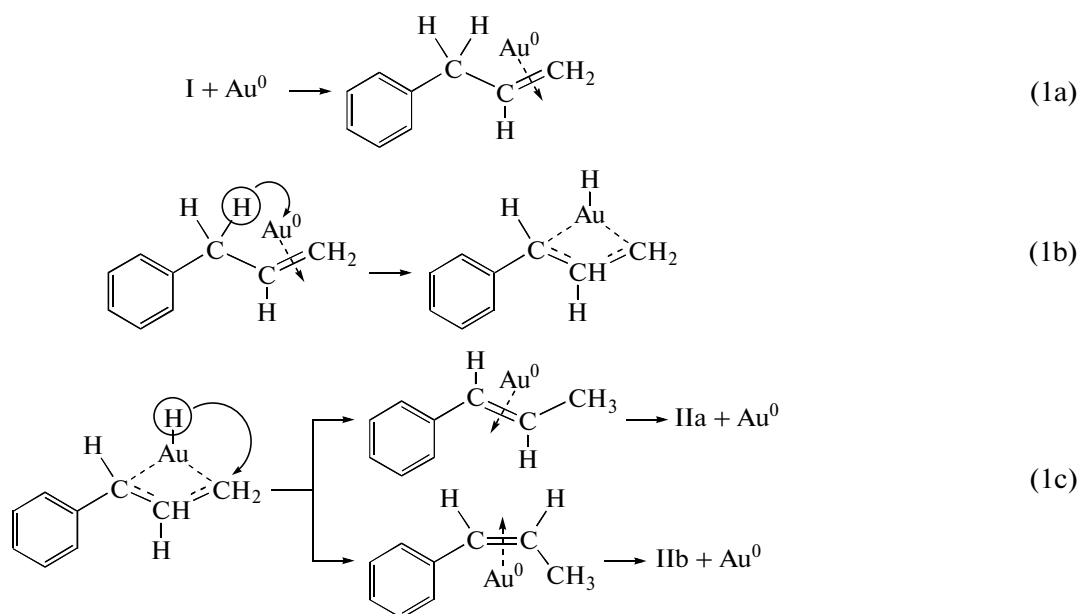
A reduction in the average size of metal particles is accompanied by a rapid rise in the isomerization rate. The size effect influences not only the activity of the catalyst, but its selectivity as well: the lower the ratio between the *trans*- and *cis*-isomers of the forming β -methylstyrene, the lower the particle size. In the range of 13 to 34 nm, e.g., the *trans/cis* ratio is 4.7 ± 0.2 ; at lower particle sizes, it falls to 2.5.

It was determined later [7] that introducing nickel at the stage of NP formation leads to a rise in the activity of gold nanoclusters during process (1) by 1–2 orders, and the nickel itself does not have measurable activity under the conditions of experiment. Further study of Au–Ni-nanocomposites allowed us to determine the correlation between the change in the bond energy of $4f_{7/2}$ -electrons of Au (E_b), the oxidation state of gold, and the rise in the catalytic activity of gold nanoclusters in reaction (1); based on this, the authors of [7] suggested the predominant role of the positively charged gold atom in this process.

In this work, we continued our study on the nature of active centers in the isomerization of allylbenzene on gold NPs and the role of positive charge on gold in process (1) by quantum chemistry.

CALCULATION METHODS

Two basic mechanisms of isomerization that assume the formation of metal–alkyl [8, 9] or metal–allyl intermediates [10, 11] were delineated. As follows from [6], the most probable mechanism of the isomerization of allylbenzene in the presence of applied gold nanoparticles Au_n and in the absence of hydrogen is metal–allylic. In this work, the metal–allylic mechanism was considered for the isomerization of allylbenzene in catalytic system ($I + \text{Au}^z$), where $z = 0, +1$:



Here, (1a) is the sorption on Au, (1b) is the formation of gold hydride complex, and (1c) is the formation of Au-β-methylstyrene complex and the desorption of β-methylstyrene.

The problem was solved by optimizing the structures of the reaction substrates; localizing and identifying the transition state (TS); and calculating the energy of the reagents, intermediates, and products of isomerization. The functional density method with a nonempirical local PBE (Perdew, Burke, Ernzerhow) functional was used as quantum-chemical method in [12–14]. Extended basis sets were used: Au [51111/51111/5111], C [311/311/11], and H [311/1], as used in the PRIRODA program [15]. The gold atom core electrons was described using the SBK pseudopotential in [16] with allowance for relativistic effects [17].

The type of the stationary points of the potential energy surface (PES) was determined from an analysis of the matrix of the second derivatives. The coordinates of the reactions were constructed according to the internal reaction coordinate [18]. The change in the thermodynamic functions in the calculated processes was determined on the basis of the statistical sums in the rigid rotor–harmonic oscillator approximation [19]. The contribution from the energy of zero oscillations was calculated in the harmonic approximation. Rate constants were calculated according to the main equation of activated complex [20].

The most important results are presented in the energy diagrams, in which the values of full energies are given with allowance for the energy of zero oscillations relative to the sum of energies of the reagents, and for the structure of the reaction substrates. One complete cycle is reflected in each diagram; the process starts with the addition of allylbenzene to the

gold atom and terminates with the desorption of allylbenzene molecule.

RESULTS AND DISCUSSION

The first step of this work was to optimize and study the PES of the reagent (allylbenzene) and the products of reaction (1) (*trans*- and *cis*-β-methylstyrene). From the PES results for torsion angle C1C2C3C4, it was determined that allylbenzene is found in the form of two conformational isomers (Fig. 1): angle 122.6° corresponds to the isomer Ia; 0° corresponds to isomer Ib, to two conformational isomers. Ia and Ib have virtually the same energy: Ib is lower in energy by 2 kJ/mol. The rotational barrier for the C2C3 bond is 10 kJ/mol, and the existence of two conformers is thus equally possible; further, we consider I to denote both isomers of allylbenzene. Optimized structures of the products of reactions IIa and IIb are given in Fig. 1.

Simulation of Allylbenzene Isomerization in the Presence of the Au⁰ Atom

An energy diagram for the formation of *trans*-isomer in the (I + Au⁰) system is shown in Fig. 2. It can be seen that the formation of *trans*-β-methylstyrene takes place in four steps. At the first stage, allylbenzene (I) forms a I₁ prereaction complex with the gold atom. The bond energy of Au–C in I₁ calculated in this work is 58.8 kJ/mol, which exceeds the experimentally determined heats of adsorption for allylbenzene on gold NPs. For example, the heat of adsorption of allylbenzene on gold particles with a size of 3 nm is 20 kJ/mol [5]. The divergence is due to a single gold atom being more coordination-unsaturated than the surface atoms of a nanoparticle.

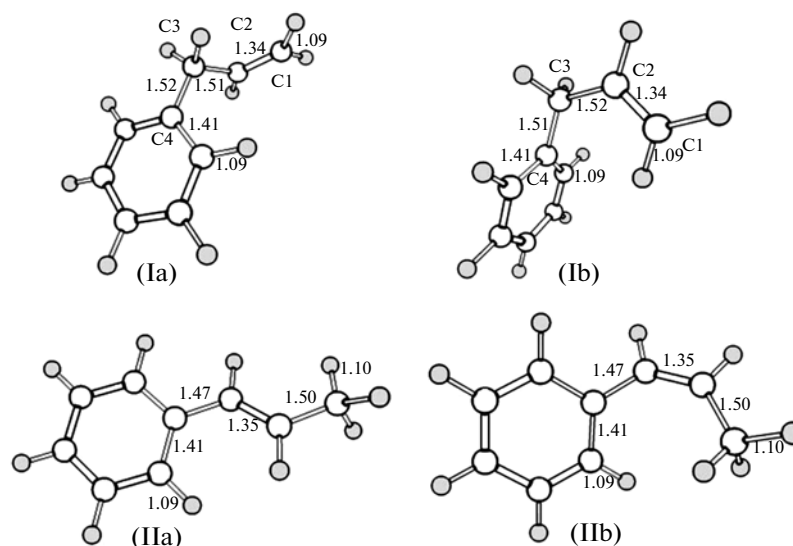


Fig. 1. Optimized structures of two conformational isomers of allylbenzene (Ia and Ib), *trans*-β-methylstyrene (IIa), and *cis*-β-methylstyrene (IIb). The corresponding carbon atoms in the structure are designated C1, C2, C3, and C4; bond lengths are given in angstroms.

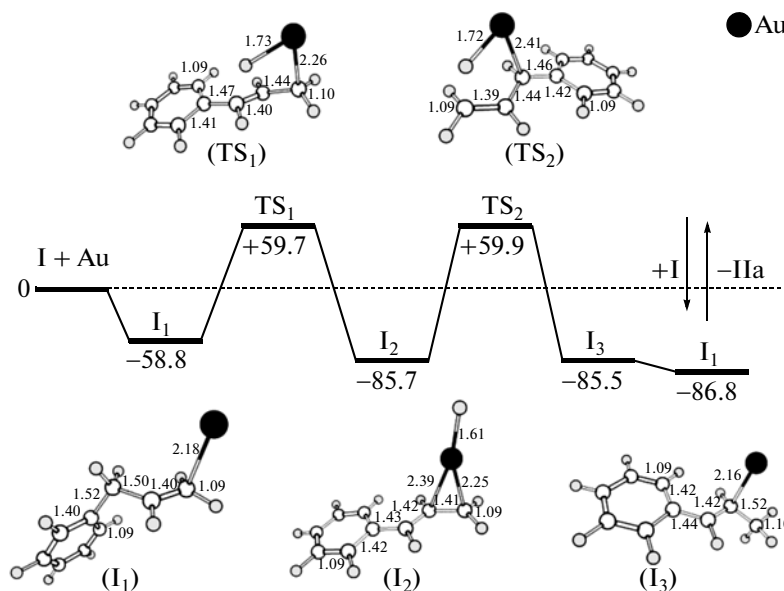


Fig. 2. Energy diagram of the reaction of the formation of *trans*-β-methylstyrene in the $I + Au^0$ system. Energies (E , kJ/mol) of all reaction substrates are given relative to the total energy of allylbenzene and Au^0 with allowance for the energy of zero oscillations; bond lengths are given in angstroms.

Intermediate complex I_1 is transformed into I_2 gold–hydride complex via the transition state (TS_1). The further transfer of hydrogen from the gold atom to the terminal carbon atom of the allylic system (C_1) results in the formation of *trans*-β-methylstyrene, connected to the gold atom (I_3). After the breakdown of the organometal bond in I_3 , *trans*-β-methylstyrene (IIa) and initial Au^0 is formed. The deliberated active center of the model of catalyst then enters the reaction again, forming a complex with allylbenzene (I_1).

The calculated values of the change in thermodynamic functions and rate constants for all stages of the formation of *cis*- and *trans*-isomers (Table 1) agree well with the data from [21]. For example, the enthalpy of the formation of *trans*-β-methylstyrene $\Delta_r H_{298}^\circ$ calculated in this work and given in [21] is -28.0 and -23.3 kJ/mol, respectively. According to Table 1, the stage of the sorption of allylbenzene ($I \rightarrow I_1$) and desorption of the product ($I_3 \rightarrow IIa$) occur without

Table 1. Thermodynamic and kinetic parameters for the reaction of the isomerization of allylbenzene on Au⁰ and Au⁺ gold atom: changes in the Gibbs energy ($\Delta_r G^\circ$, kJ/mol), enthalpy ($\Delta_r H^\circ$, kJ/mol), entropy ($\Delta_r S^\circ$, J/(mol K)), activation energy (E_0 , kJ/mol), and the rate constant (k , s⁻¹)

Stage	$\Delta_r G^\circ$	$\Delta_r H^\circ$	$\Delta_r S^\circ$	E_0	k
Allylbenzene + Au ⁰ = <i>trans</i> - β -methylstyrene + Au ⁰					
I + Au ⁰ $\longrightarrow$ I ₁	-75.3	-52.5	76.5	—	—
I ₁ $\longrightarrow$ I ₂ (TS ₁)	-33.0	-37.9	-16.4	118.5	4.9×10^{-10}
I ₂ $\longrightarrow$ I ₃ (TS ₂)	11.0	10.5	-1.5	145.6	5.5×10^{-13}
I ₃ $\longrightarrow$ IIa + Au ⁰	68.2	50.8	-56.0	—	—
Allylbenzene + Au ⁰ = <i>cis</i> - β -methylstyrene + Au ⁰					
I + Au ⁰ $\longrightarrow$ I ₄	-70.1	-51.0	64.4	—	—
I ₄ $\longrightarrow$ I ₅ (TS ₃)	-21.2	-24.6	-11.3	133.5	3.2×10^{-12}
I ₅ $\longrightarrow$ I ₆ (TS ₄)	6.2	8.2	8.6	144.9	2.3×10^{-13}
I ₆ $\longrightarrow$ IIb + Au ⁰	71.5	-51.8	66.0	—	—
Allylbenzene + Au ⁺ = <i>trans</i> - β -methylstyrene + Au ⁺ (route 1)					
I + Au ⁺ $\longrightarrow$ I ₇	-445.1	-309.9	453.4	—	—
I ₇ $\longrightarrow$ I ₈ (TS ₅)	-16.2	-19.9	-12.5	92.2	8.5×10^{-5}
I ₈ $\longrightarrow$ I ₁₁ (TS ₆)	-56.4	-58.8	-8.0	100.8	4.4×10^{-6}
I ₁₁ $\longrightarrow$ IIa + Au ⁺	484.1	358.1	-422.8	—	—
Allylbenzene + Au ⁺ = <i>trans</i> - β -methylstyrene + Au ⁺ (route 2)					
I + Au ⁺ $\longrightarrow$ I ₇	-445.1	-309.9	453.4	—	—
I ₇ $\longrightarrow$ I ₈ (TS ₅)	-16.2	-19.9	-12.5	92.2	8.5×10^{-5}
I ₈ $\longrightarrow$ I ₉ (TS ₇)	-22.2	-23.2	-3.3	39.3	2.9×10^5
I ₉ $\longrightarrow$ I ₁₀ (TS ₈)	51.2	55.1	13.0	68.3	2.8×10^2
I ₁₀ $\longrightarrow$ I ₁₁	-85.4	-90.7	-17.8	—	—
I ₁₁ $\longrightarrow$ IIa + Au ⁺	484.1	358.1	-422.8	—	—
Allylbenzene + Au ⁺ = <i>trans</i> - β -methylstyrene + Au ⁺ (route 3)					
I + Au ⁺ $\longrightarrow$ I ₁₂	-436.3	-306.1	-194.6	—	—
I ₁₂ $\longrightarrow$ I ₁₃ (TS ₉)	-4.9	-8.0	-10.2	94.2	5.6×10^{-5}
I ₁₃ $\longrightarrow$ I ₁₁ (TS ₁₂)	-70.9	-71.9	-3.4	100.1	2.0×10^{-5}
I ₁₁ $\longrightarrow$ IIa + Au ⁺	484.1	358.1	-422.8	—	—
Allylbenzene + Au ⁺ = <i>cis</i> - β -methylstyrene + Au ⁺					
I + Au ⁺ $\longrightarrow$ I ₁₂	-436.3	-306.1	-194.6	—	—
I ₁₂ $\longrightarrow$ I ₁₃ (TS ₉)	-4.9	-8.0	-10.2	94.2	5.6×10^{-5}
I ₁₃ $\longrightarrow$ I ₁₄ (TS ₁₀)	-4.1	-6.3	-7.2	28.9	3.3×10^7
I ₁₄ $\longrightarrow$ I ₁₅ (TS ₁₁)	-8.1	-8.1	11.1	6.9	3.7×10^{11}
I ₁₅ $\longrightarrow$ I ₁₆ (TS ₁₃)	48.3	51.0	9.1	66.6	2.0×10^{-2}
I ₁₆ $\longrightarrow$ I ₁₇	-96.7	-101.2	-15.2	—	—
I ₁₇ $\longrightarrow$ IIb + Au ⁺	488.2	360.1	-429.6	—	—

Note: The temperature was 298.15 K. The reagents in the stages are identified in Figs. 2–5.

barriers, while the step of the formation of the reaction intermediates have activation energies of 118.5 and 145.6 kJ/mol, respectively. The rate constant of the limiting stage (I₂ $\longrightarrow$ I₃) is 5.5×10^{-13} s⁻¹.

The stages of the formation of *cis*- β -methylstyrene in the I + Au⁰ system are analogous to those described for *trans*- β -methylstyrene. At the same time, the

energy profiles of the formation of *trans*- and *cis*- isomer in the I + Au⁰ system are a bit different. For example, the calculated bond energy of Au–C in the prereaction complex I₄ is 57.0 kJ/mol (Table 1), in contrast to 58.8 kJ/mol in I₁ (Fig. 2); the energy barrier of the formation of the intermediate hydride complex in the case of *cis*-isomer (TS₃) is 15 kJ/mol larger than for the

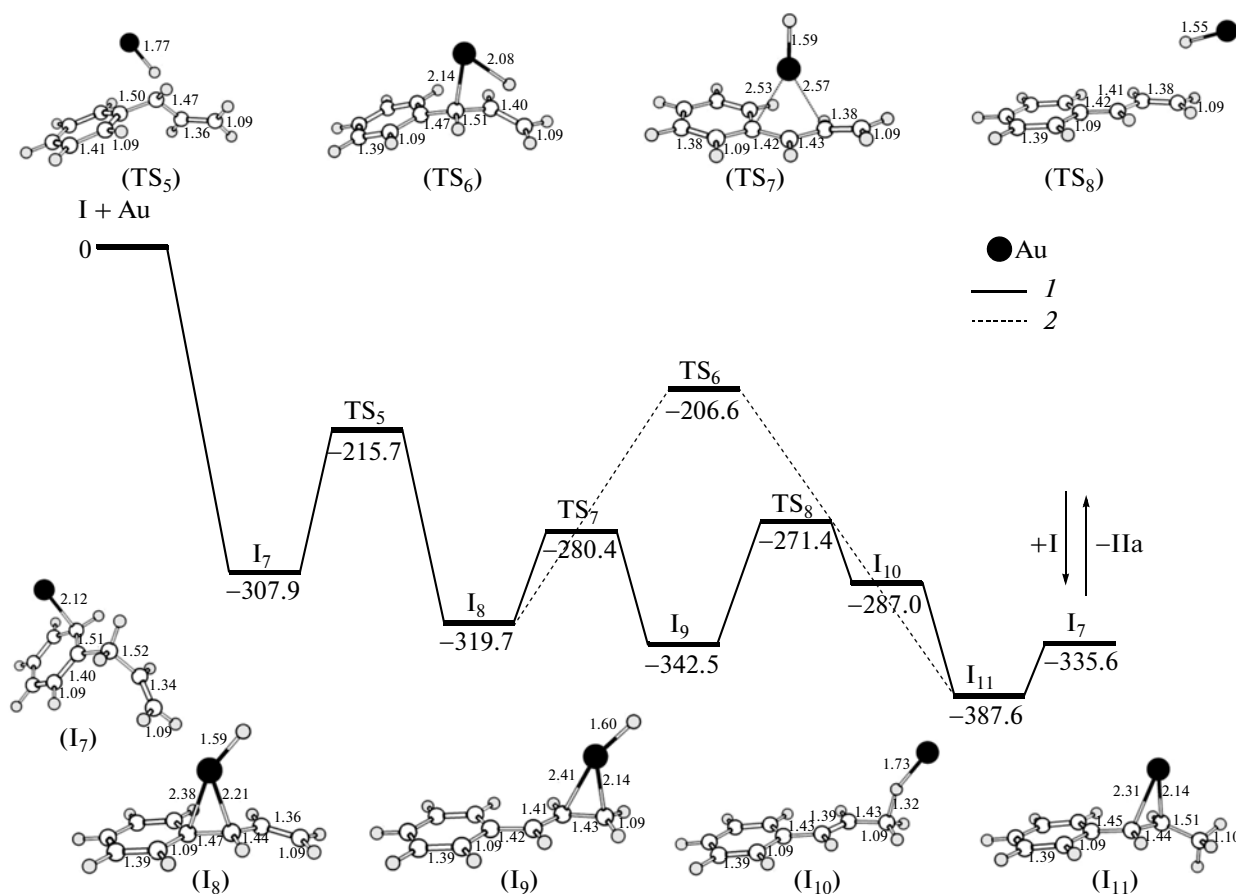


Fig. 3. Energy diagram for the formation of *trans*- β -methylstyrene in the $I + Au^+$ system. Energies (E , kJ/mol) of all reaction substrates are given relative to the total energy of allylbenzene and Au^+ with allowance for the energy of zero oscillations; bond lengths are given in angstroms. (1) represents route 1; (2), route 2.

trans- product. It is interesting to note that the rate constant of the limiting stage in the formation of *cis*-isomer ($I_5 \rightarrow I_6$) is $2.32 \times 10^{-13} \text{ s}^{-1}$; this is half the rate constant of the limiting stage of the formation of *trans*-isomer ($I_2 \rightarrow I_3$) (Table 1).

Simulating the Isomerization of Allylbenzene in the Presence of the Au^+ Ion

As was mentioned above, there is a substantial increase in the rate of the isomerization of allylbenzene in the presence of positively charged gold ions on the surface. The next step in researching reaction (1) was to simulate the $I + Au^+$ catalytic system. The energy diagrams and optimized structures of the reaction substrates for this case are given in Figs. 3 and 4. The calculated values for the change in the thermodynamic functions and rate constants for all stages in the formation of *cis*- and *trans*-isomer in the $I + Au^+$ system are presented in Table 1.

As in the $I + Au^0$ system, a complex of allylbenzene with Au^+ ion is formed (I_7) (Fig. 3) at the first stage of the reaction leading to *trans*- β -methylstyrene in the

$I + Au^+$ system, with a higher energy advantage than I_1 ($\Delta_r G^\circ(I_7) = -445.1 \text{ kJ/mol}$, $\Delta_r G^\circ(I_1) = -70.1 \text{ kJ/mol}$). This is explained by the formation of a stronger bond between the electron-deficient gold ion and the π -system of the benzene ring. According to the energy diagram (Fig. 3), the approach to the formation of *trans*- β -methylstyrene assumes two gold-hydride intermediates (I_8 and I_9) that differing by the coordination of gold in the allylic system. In complex I_8 , the bonding is accomplished with a carbon atom in the benzene ring (C4 and C3); in the case of complex I_9 , the bonding takes place on the terminal carbon atoms (C1 and C2). Complex I_9 is more stable than complex I_8 by 23.8 kJ/mol. Due to the existence of I_9 , several ways of $I_8 \rightarrow I_{11}$ transformation (and thus two possible ways of isomerization) are possible (Fig. 3).

The first route, $I_7 \rightarrow II_a$, passes only through the intermediate I_8 state and two transition states (TS_5 and TS_6); the activation energies of the corresponding stages are 92.0 and 100.8 kJ/mol, respectively. The rate constant of the limiting stage of ($I_8 \rightarrow I_{11}$) is $4.4 \times 10^{-6} \text{ s}^{-1}$.

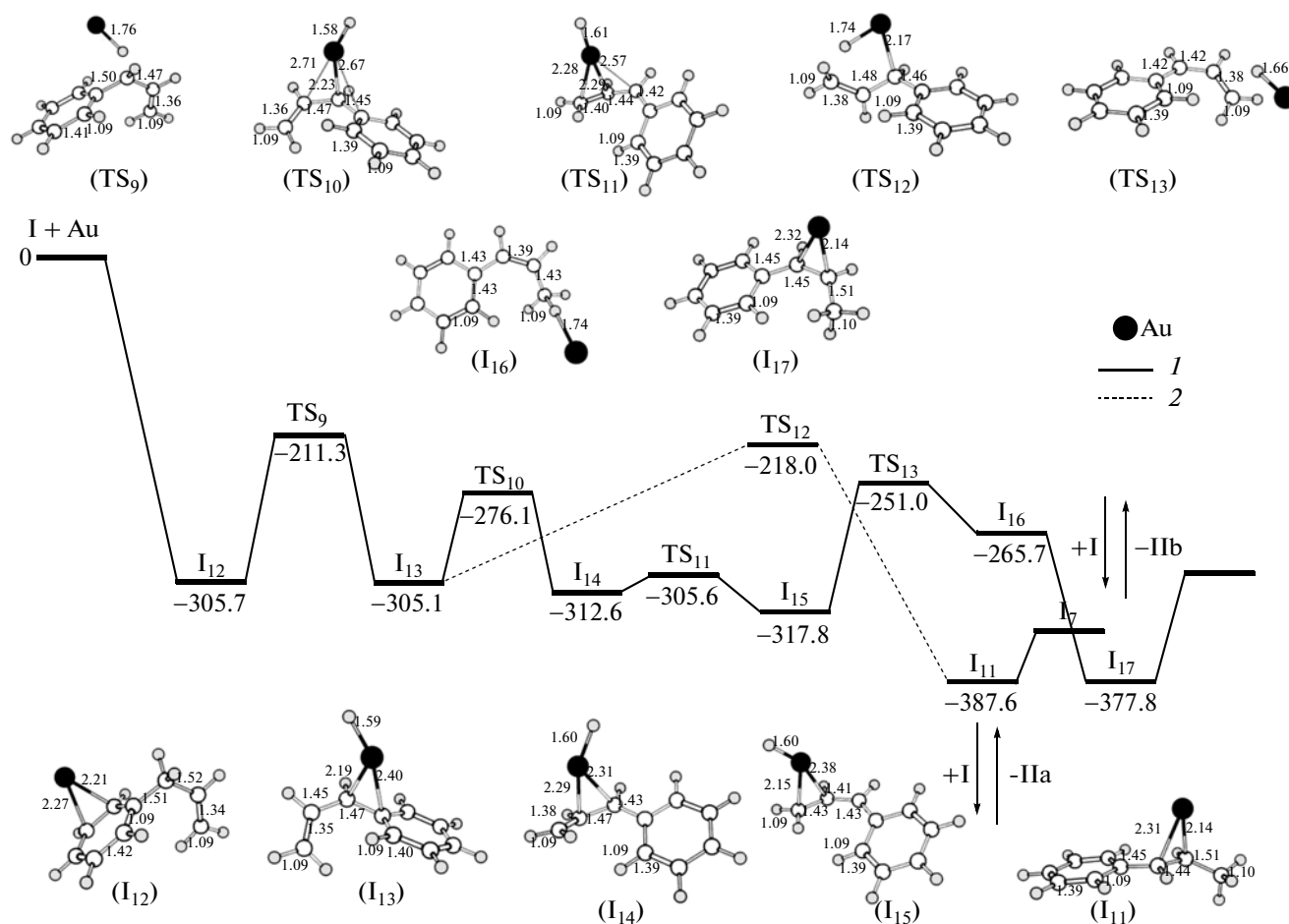


Fig. 4. Energy diagram for the formation of *cis*- β -methylstyrene in the $I + Au^+$ system. Energies (E , kJ/mol) of all reaction substrates are given relative to the total energy of allylbenzene and Au^+ with allowance for the energy of zero oscillations; bond lengths are given in angstroms. (1) represents the formation of IIb; (2), the formation of IIa, route 3.

The second route, $I_7 \rightarrow IIa$, passes through the intermediate I_8 and I_9 states and three transition states (TS_5 , TS_7 , and TS_8), and the values of potential barriers of the last two stages decline and correspond to 39.3 and 68.3 kJ/mol. The rate constant of the limiting stage via the second route ($I_7 \rightarrow I_8$) is $8.5 \times 10^{-5} s^{-1}$. Regardless of the route at the final stage, we observe the formation of the less stable *trans*- β -methylstyrene- Au^+ complex (I_{10}), which transitions to the more stable I_{11} complex with an energy advantage of 100.6 kJ/mol. Desorption of the *trans*- β -methylstyrene product takes place from I_{10} or I_{11} ; in the latter case, 359.9 kJ/mol is required. The second route of *trans*- β -methylstyrene formation, via the intermediates I_8 and I_9 , is consequently the most appropriate.

According to Table 1, the rate constant of the limiting stage of *trans*-isomer formation in the $I + Au^+$ system is $8.5 \times 10^{-5} s^{-1}$; in the $I + Au^0$ system, it is only $5.5 \times 10^{-13} s^{-1}$. This increase in the reaction rate confirms the hypothesis regarding the active centers of $Au^{\delta+}$ proposed in [7]. A multiple-step mechanism for

the formation of *cis*- β -methylstyrene was discovered (Fig. 4) that includes the formation of three gold-hydride complexes (I_{13} , I_{14} , and I_{15}) on the PES. The transition from one gold-hydride complex to another occurs via the displacement of Au-H along the allyl system. Notably, no hydride complex similar to I_{14} was detected in the previous systems. The rate constant of the limiting stage is $5.6 \times 10^{-5} s^{-1}$ (stage $I_{12} \rightarrow I_{13}$).

Another route of the transformation of I_{13} is possible, however; not to I_{14} , but to the *trans*- β -methylstyrene- Au^+ (I_{11}) complex via the potential barrier of 100.1 kJ/mol (TS_{12}). It is evident that the first stage of the formation of intermediate I_{13} via two routes is the same and is limiting; the two directions, $I_{13} \rightarrow I_{11}$ and $I_{13} \rightarrow I_{16}$, are therefore considered equally possible and competing. The possibility of the additional accumulation of *trans* in the system thus arises.

It should be noted that the rate constant of the limiting stage of the formation of *cis*-isomer in the presence of Au^+ is $5.6 \times 10^{-5} s^{-1}$ and lower than the rate of the limiting stage of the formation of *trans*-isomer

Table 2. Physicochemical properties of M/X (M = Au, Ni, Au–Ni, X = SiO₂, C) nanocomposites and their activity during the isomerization of allylbenzene, according to [7]

Parameter	Au–Ni/SiO ₂	Au–Ni/SiO ₂	Ni/SiO ₂	Au/SiO ₂	Au/C
Ni, wt %	0.10	0.16	0.30	—	0.46
Au, wt %	0.14	0.40	—	0.21	0.45
<i>d</i> , nm	3 and 45	3 and 45	50	3	3
<i>E</i> ₁ , eV	856.0	856.7	855.9	—	—
<i>E</i> ₂ , eV	84.3	84.2	—	84.1	84.0
β ₁	+2	+2	+2	—	—
β ₂	δ+	δ+	—	δ+	0
<i>a</i>	5583	4624	0	108	0.1

Note: *d* is the diameter of applied particles; *E*₁ and *E*₂ are the bond energies of electrons in Ni 2*p*_{3/2} and Au 4*f*_{7/2}, respectively; β₁ and β₂ are the oxidation states of Ni and Au, respectively; and *a* is the activity of Au nanoparticles. Mol allylbenzene (mol Au)^{−1} h^{−1}.

(8.5 × 10^{−5} s^{−1}). The observed difference in the reaction rates, along with the additional possible ways of the formation of *trans*-product, confirm the selective formation of *trans*-isomer during the isomerization of allylbenzene in I + Au⁺ system, and is in good agreement with experimental kinetic studies of allylbenzene isomerization in the presence of gold nanoparticles [6].

*Effect of the Positive Charge
on the Activity of Gold Nanoparticles
during the Isomerization of Allylbenzene*

Some physicochemical and catalytic properties of gold and nickel nanoparticles during the allylic isomerization at 170°C obtained in [7] are given in Table 2. As follows from a comparison of the bond energies of Ni 2*p*_{3/2} electrons in the obtained systems with the bond energies in the nickel compounds of various valent state [7], nickel preferentially takes the form of NiO in the samples under study. It is the reason of its zero activity during the isomerization of allylbenzene. On the other hand, as it follows from Table 2 the catalytic activity of the gold clusters correlates with the binding energy of the Au 4*f*_{7/2} core electrons. Considering that *E*_b(4*f*_{7/2}) = 84.7 eV corresponds to the clusters (Au_{*n*})^{δ+}, and *E*_b(4*f*_{7/2}) = 84.0 eV to the clusters (Au_{*n*})⁰ [22], we may conclude that the catalytic activity of gold nanoclusters increases with an increase in their positive charge.

Another evidence of the advantage of the charged gold clusters in the reaction [7]: It was discovered that the immobilization of gold nanoparticles on a carbon support, which undoubtedly occurs with no change in the valent state of the metal or the appearance of a noticeable charge on the nanoparticles, prevents us from obtaining active catalysts, as the activity of gold clusters is close to zero on this support. Silicon oxide has acidic –(OH) Brønsted centers on its surface, while there are acidic Al³⁺ Lewis centers in addition to

Brønsted centers on the surface of aluminum oxide. According to [2, 23], the immobilization of gold on these leads to the appearance of a positive charge that is in turn manifested in the high activity of Au/SiO₂ and Au/Al₂O₃ during the isomerization of allylbenzene [6, 7].

CONCLUSIONS

Comparing the data of Tables 1 and 2, we may conclude that the rise in the rate of isomerization upon the transition from Au⁰ to Au⁺ obtained in this work agrees well quantitatively with the experimentally determined dependence for the catalytic activity of the gold nanoclusters on its oxidation state.

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