Density functional study of ethylene polymerization on zirconocene catalysts
2.* Substituted zirconocene catalysts

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Polymerization of ethylene on zirconocene catalysts was studied with the density functional theory. The approach proposed previously for the model system $Cp_2ZrEt^+ + C_2H_4$ was extended to substituted zirconocene catalysts $(RCp)_2ZrEt^+$, which allowed us to compare the results of calculations with the experimentally found rate constants of chain propagation. The ethyl fragment was demonstrated to be an adequate model for a growing polymer chain. The order of decrease in the activation energy of chain propagation calculated for compounds with R = H, Me, Pr^n, and Bu^n is in qualitative agreement with the experimental data. However, the quantitative description gave underestimated theoretical rate constants of chain propagation compared to the experimental values. In the case of polyalkyl-substituted zirconocenes (R = 1,2-Me_2 or Me_4), no correlation between the calculated and experimental characteristics was observed. The results were explained using the simplest model reaction of the replacement of the $MeMAO^-$ counterion by an ethylene molecule accompanied by displacement of the former to the outer coordination sphere of the Zr atom. This step was demonstrated to control the kinetics of the process. It was concluded that the isolated-cation model used in early investigations is not adequate and calls for modification with regard to the effect of the counterion.

Key words: polyolefins, substituted zirconocenes, quantum-chemical calculations, density functional theory.

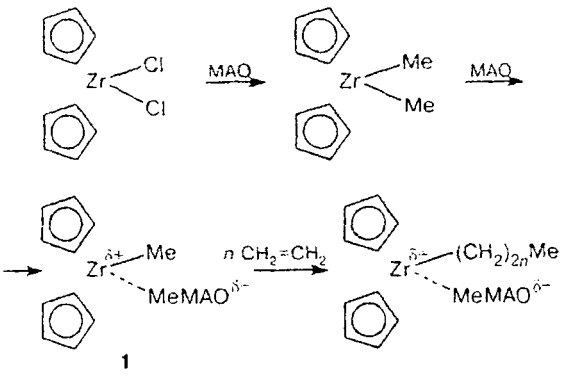
Quantum-chemical calculations find increasing application in studies of mechanisms of catalytic processes, in particular, of olefin polymerization on zirconocene catalysts. The application of the functional density theory[2–6] made it possible to substantially increase the sizes of the systems under investigation (up to tens of atoms with the use of 1000 and more basis functions) and to perform quantitative comparison of the results of quantum-chemical calculations with the data from kinetic studies. In the present work, we carried out such comparison for a series of alkyl-substituted zirconocenes.

It is commonly accepted that ion pair **1** is a species catalyzing polymerization of terminal olefins. In real catalytic systems, ion pairs **1** are as a rule generated by the treatment of dichlorozirconocene with a large excess of methylalumoxane (MAO). In this case, zirconocene is initially methylated followed by the formation of an adduct (**1**) of Cp_2ZrMe_2 with MAO, which directly reacts with olefin and initiates its polymerization[7] (Scheme 1).

The weakly nucleophilic anion $MeMAO^-$ is an alumoxane globule with an unknown structure of stoichiometric composition $(AlOMe)_n$.

It was suggested that the general scheme of the catalytic cycle involves two major steps, *viz.*, the reaction of the catalyst with an ethylene molecule to form an

Scheme 1



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intermediate complex in which Alkyl designates a growing polymer chain (reaction (1)) and isomerization of this intermediate, leading to a polymer chain elongated by a monomer unit (reaction (2)).

Up to now, step (2) has been considered as the rate-determining reaction stage in all theoretical studies. In particular, this conclusion was made in the theoretical studies[2–6] in which the model system $\{Cp_2ZrEt^+ + C_2H_4\}$ was examined in detail with the use of the density functional theory. In the previous communication,[1] we have confirmed the qualitative conclusions made in the

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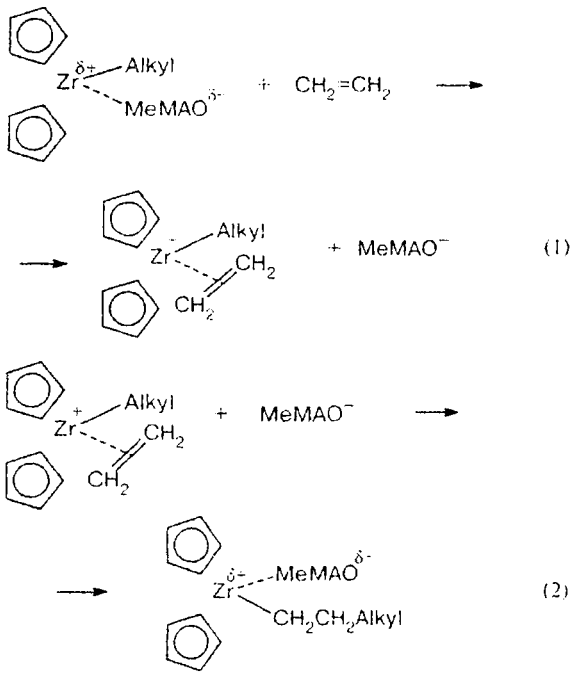
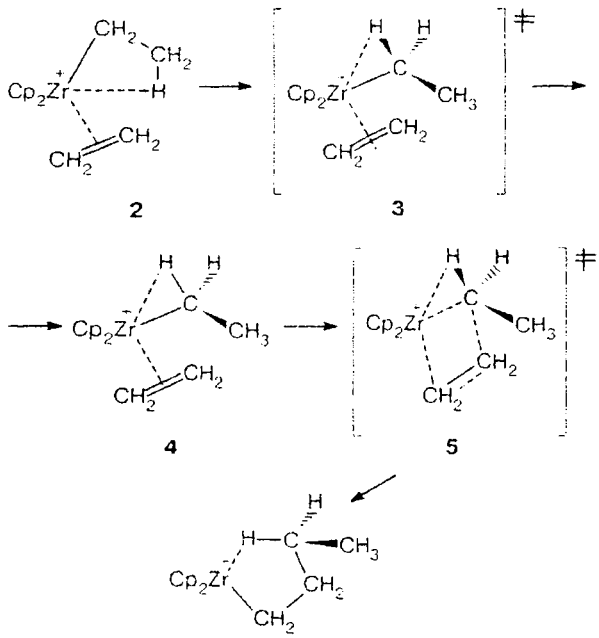


cited works by studying the same system with the use of the PBE density functional and extended basis sets.

Scheme 2



It was demonstrated[2–6] that the major channel of polymer chain propagation involves the conversion of β-agostic adduct **2** into α-agostic complex **4** followed by the insertion of an ethylene molecule at the Zr—C bond through transition state **5** to form γ-agostic product **6**. Transition state **5** is either characterized by a noticeably lower energy than that of **3**[6] or not localized on the potential energy surface of the system at all.[1,4] In the latter case, the reaction proceeds without a barrier and, hence, has no effect on the kinetics of chain propagation. Complex **2** is converted into compound **4** through transition state **3** with cleavage of the β-agostic bond accompanied by rotation of the ethyl group about the Zr—C bond. In this connection, we estimated the activation energy of chain propagation as the difference between the energies of transition state **3** and complex **2**.

Apparently, interactions within the contact ion pair $Cp_2ZrAlkyl^+MeMAO^-$ cannot be ignored in real catalytic systems. The reaction with ethylene is accompanied by replacement of the $MeMAO^-$ counterion to the outer coordination sphere of Zr. If the Me^- anion is used as the simplest model of $MeMAO^-$, the ability of zirconocene to add ethylene giving rise to a separated ionic pair may be characterized by the free activation energy (ΔG_{298}) of the reaction

$$(RCp)_2Zr(Et)Me + C_2H_4 \rightleftharpoons \rightleftharpoons [(RCp)_2Zr(Et)C_2H_4]^+ + Me^- \quad (3)$$

The aim of this work was to examine the agreement between the results of theoretical studies[1–6] and the experimental kinetic parameters determined previously[8] for a series of alkyl-substituted zirconocene catalysts. This comparison allows one to evaluate the correctness of the description of a real catalytic system by the model of an isolated cation.

Calculation procedure

All calculations were carried out as described previously.[1] We used the density functional, which includes the electron density gradient.[9] The program used in calculations involves Gaussian basis sets for solving the Kohn—Sham equations and the expansion of the electron density in an auxiliary basis set.[10] The following contracted orbital basis sets were used: (5s1p)/[3s1p], (11s6p2d)/[6s3p2d], and (21s16p12d)/[15s12p7d] for H, C, and Zr, respectively. The auxiliary basis sets consisted of uncontracted Gaussian functions of dimensions (5s1p), (10s3p3d1f), and (21s9p9d8f8g) for H, C, and Zr, respectively. In the optimization of the geometry, no constraints were imposed on the local symmetry. The type of stationary points was determined by analytical calculations of second derivatives of the energy.

Results and Discussion

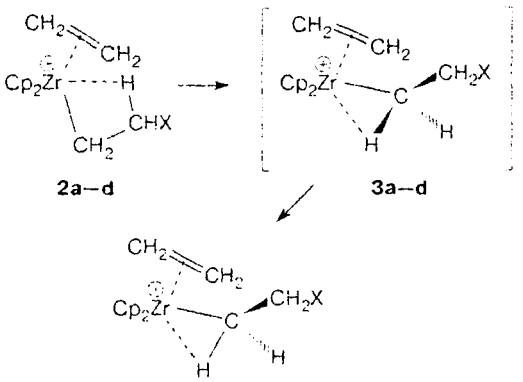
Choice of a model for a growing polymer chain

In studies of the unsubstituted zirconocene catalyst,[1–6] no consideration has been given to the choice of a hydrocarbon fragment as a model of a growing polymer chain such that calculations would ensure the independence of the final results of calculations from the length of this fragment. However, this problem is of

fundamental importance in discussion of quantitative characteristics of the catalyst.

Using the unsubstituted alkylzirconocene cation as an example, we considered the question of whether the difference between the energies of **3** and **2** depends on the type of the alkyl group (Et, Pr, Bu, *etc.*) bound to the metal atom. In the previous studies, either Me [1] or CH_3Me [2–6] were chosen as models of a growing polymer chain, which, in principle, may be inadequate to correctly describe the process.

Scheme 3



X = H (**a**), Me (**b**), Et (**c**), Pr (**d**)

The activation energies of the rearrangement of complex **2** into complex **4** through transition state **3** calculated for different alkyl groups bound to the Zr atom (X = H, Me, Et, or Pr) are given in Table 1. As can be seen from Table 1, the ΔE values increase only slightly as the chain length increases. However, a simultaneous increase in the entropy of activation ΔS_{298} compensates for this effect and the ΔG_{298} value for the reaction is virtually independent of the chain length. Therefore, the use of the ethyl group (X = H) as a model of the polymer chain for solving the above-mentioned problem seems to be reasonable. Hereinafter we will use this approximation.

Reactions of dialkyl-substituted ethylzirconocene cations $[(RCp)_2ZrEt]^+$ (R = Me, Pr^n, or Bu^n) with an ethylene molecule

Investigation of the mechanism of the reaction of ethylzirconocene cations (R = Me, Pr^n, or Bu^n) with an ethylene molecule demonstrated that in all cases the structures of intermediates and transition states (including the mutual orientation of the substituents in the Cp rings) are very similar and only the quantitative characteristics of the reaction change in this series. Hence, all possible intermediate structures appearing in the course of the transformation of complex **2** into **4** can be considered in detail using the $[(MeCp)_2ZrEt]^+$ cation as an example.

Table 1. Activation energies and thermodynamic parameters of transition states **3** of isomerization of β-agostic complex **2** into **4**.

R	ν_{imag} /cm^{-1}	ΔE	ΔH_0	ΔH_{298}	ΔG_{298}	ΔS_{298}
		kcal mol^{-1}				/cal mol^{-1} K^{-1}
H	173i	5.20	3.86	3.98	3.66	1.09
Me	150i	5.25	3.96	4.07	3.46	2.05
Et	152i	5.36	4.02	4.15	3.44	2.39
Pr	152i	5.51	4.17	4.30	3.55	2.52

Note. The image frequencies (ν_{imag}), the activation energies without considering the zero-point energies (ΔE) and taking into account these energies (ΔH_0), the enthalpies of activation (ΔH_{298}), the entropies of activation (ΔS_{298}), and the free activation energies (ΔG_{298}) for transition states **3** of isomerization of β-agostic complex **2** into **4**.

Structures and energies of intermediates of $[(MeCp)_2Zr(Et)C_2H_4]^+$. Stationary points corresponding to four β-agostic complexes $[(MeCp)_2Zr(Et)C_2H_4]^+$ (**7a–d**), which differ in the mutual arrangement of the Me groups, were located on the potential energy surface of the $[(MeCp)_2ZrEt]^+ + C_2H_4$ system. Their structures are shown in Fig. 1. The thermodynamic characteristics of the complexes are given in Table 2. The relative energies (ΔE) of **7a–d** are 0, 0.06, 0.16, and 0.47 kcal mol^{-1}, respectively. The differences in the energy of the optimized structures are small and comparable with the energy of thermal motion at ~20 °C (~0.6 kcal mol^{-1}). The standard ΔG_{298} values increase in the series of complexes **7a–d** in parallel with an increase in the energy. Hence, it is appropriate to consider compounds **7a** and **7b**, possessing the lowest energies, as the initial states.

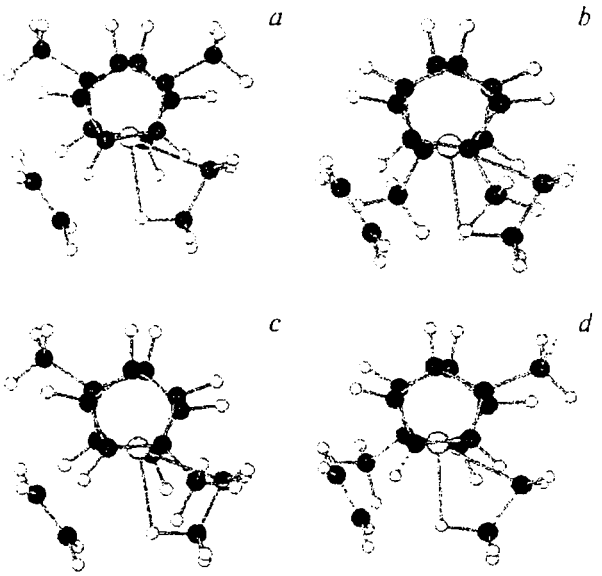


Fig. 1. Structures of the complexes $[(MeCp)_2Zr(C_2H_4)Et]^+$: **7a** (*a*), **7b** (*b*), **7c** (*c*), and **7d** (*d*).

Table 2. Energies and thermodynamic parameters of the conformers of β-agostic complex **7**, $[(MeCp)_2Zr(Et)C_2H_4]^+$

Compound	ΔE	ΔH_0	ΔH_{298}	ΔG_{298}	ΔS_{298}
	kcal mol^{-1}				/cal mol^{-1} K^{-1}
7b	0.06	0.17	0.11	0.20	−0.33
7c	0.16	0.20	0.26	0.29	−0.43
7d	0.47	0.59	0.50	0.50	−0.02

Note. The parameters are given relative to conformer **7a**, for which all values presented in the table are taken as zero.

Structures and energies of transition states of the reaction $[(MeCp)_2ZrEt]^+ + C_2H_4$. The general set of transitions states **8a—f** in the course of chain propagation (Fig. 2) corresponds to complexes **7a** and **7b**. The energies of **8a—f** are 4.7, 5.3, 5.5, 5.7, 5.8, and 6.2 kcal mol^{-1}, respectively. The energies and the thermodynamic parameters of transition states **8a—f** are given in Table 3.

As can be seen from Table 3, transition state **8a** is characterized by the lowest energy. Hence, this transition state would be expected to play the key role in the model reaction under consideration. The activation energy ΔH_0 of state **8a** (3.8 kcal mol^{-1}) is virtually identical to the ΔH_0 value for the reaction of the unsubstituted ethylzirconocene cation (3.98 kcal mol^{-1}; compound **3** in Table 3). A comparison of the calculated ΔG_{298} values demonstrated that transition state **8e** is characterized by the lowest free energy. Calculations of vibration frequencies and, consequently, of entropies of such complex systems in the harmonic approximation can give erroneous results. Therefore, the ΔG_{298} values given in Table 3 can be considered only as approximate values for real catalysts. However, the probability of the results being erroneous decreases in the case of examination of the overall range of the values ΔG_{298}(**8a**)—ΔG_{298}(**8e**).

The reactions of $[(RCp)_2ZrEt]^+$ (R = Pr^n or Bu^n) with an ethylene molecule. The energies and thermodynamic characteristics of intermediate complexes and transition states for other dialkyl-substituted (R = Pr^n or Bu^n) zirconocenes (Table 4) were calculated analogously.

The enthalpies of activation ΔH_0 for isomerization of β-agostic adduct **2** to form α-agostic complex **4** change in the series 3.9 (R = H), 3.8 (R = Me, **8a**), 3.7 (R = Pr^n, **8a**), and 3.5 kcal mol^{-1} (R = Bu^n, **8a**). The standard ΔG_{298} values change in the same series as follows: 3.7 (R = H), 3.3—3.6 (R = Me, **8a—e**), 3.3—3.5 (R = Pr^n, **8a—e**), and 2.9—3.1 kcal mol^{-1} (R = Bu^n, **8a—e**). At 326 K, the calculated ΔG_{326} values are 3.6

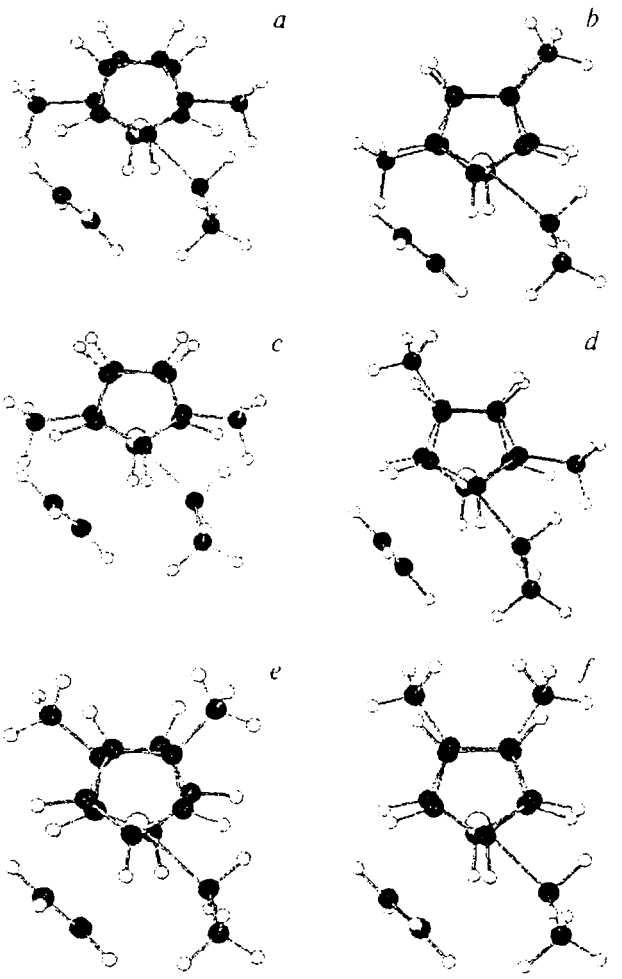


Fig. 2. Structures of transition states **8** of isomerization of the complexes $[(MeCp)_2Zr(C_2H_4)Et]^+$: **8a** (*a*), **8b** (*b*), **8c** (*c*), **8d** (*d*), **8e** (*e*), and **8f** (*f*).

Table 3. Energies and thermodynamic parameters of transition states **8a—f** of chain propagation in the case of Me-substituted zirconocene catalysts

Compound	ν_{imag} /cm^{-1}	ΔE	ΔH_0	ΔH_{298}	ΔG_{298}	ΔS_{298}
		kcal mol^{-1}				/cal mol^{-1} K^{-1}
3	173i	5.20	3.86	3.98	3.66	1.09
8a	146i	4.89	3.79	3.76	3.61	0.49
8b	179i	5.43	4.31	4.33	3.92	1.29
8c	162i	5.54	4.41	4.41	4.03	1.30
8d	153i	5.71	4.56	4.56	4.04	1.76
8e	162i	5.82	4.75	4.75	3.31	4.84
8f	164i	5.82	4.77	4.77	4.81	−0.14

Note. For states **3**, the values are given relative to complex **2**; for state **8a—f**, the values are given relative to **7a**.

Table 4. Energies and thermodynamic parameters of the conformers of β-agostic complex **7**, $[(RCp)_2Zr(Et)C_2H_4]^+$, and of transition states **8a** and **8e** of chain propagation in the case of Pr- and Bu-substituted zirconocene catalysts

Compound	ν_{imag} /cm^{-1}	ΔE	ΔH_0	ΔH_{298}	ΔG_{298}	ΔS_{298}
		kcal mol^{-1}				/cal mol^{-1} K^{-1}
			R = Pr			
7b	—	−0.05	0.13	0.04	0.28	−0.81
8a	143i	4.81	3.71	3.74	3.47	0.92
8e	153i	5.62	4.38	4.54	3.27	4.26
			R = Bu			
7b	—	−0.06	0.04	−0.01	0.00	−0.03
8a	137i	4.77	3.50	3.59	3.09	1.66
8e	150i	5.58	4.25	4.48	2.95	5.12

Note. The parameters are given relative to conformer **7a**, for which all values presented in the table are taken as zero.

(R = H), 3.2—3.6 (R = Me, **8a—e**), 3.2—3.4 (R = Pr^n, **8a—e**), and 2.8—3.1 kcal mol^{-1} (R = Bu^n, **8a—e**), which are very similar to the standard values.

Therefore, according to the experimental data,[8] the rate constant of chain propagation should increase on going from the usubstituted complex to the butyl-substituted derivative.

Within the framework of the absolute reaction rate theory,[12] the rate constant of a monomolecular reaction is proportional to $\exp(-\Delta G^{\neq}/RT)$. Then, with the rate constant for the unsubstituted zirconocene catalyst taken as unity, the calculated rate constants of chain propagation at 326 K are 1 (H), 1.0—2.0 (Me), 1.3—2.1 (Pr^n), and 2.4—3.5(Bu^n), whereas the ratio between the experimental values[8] is 1 (H) : 1.3 (Me) : 9.7(Pr^n) : 11.7 (Bu^n). From these findings we conclude that the quantitative description gave underestimated rate constants of chain propagation for R = Pr^n or Bu^n compared to the corresponding experimental values. Apparently, there is at least one more parameter controlling the kinetics of the process other than the energy of isomerization of β-agostic complex **7** into the corresponding α-agostic complex through transition state **8**.

Reactions of polymethyl-substituted ethylzirconocene cations $[(Me_nCp)_2ZrEt]^+$ (n = 2 or 4) with an ethylene molecule

Let us examine whether calculations provide reliable predictions of the properties of the polyalkyl-substituted ethylzirconocene cations $[(Me_nCp)_2ZrEt]^+$ (n = 2 or 4).

Structures and energies of intermediates and transition states of the reaction $[(1,2\text{-}Me_2Cp)_2ZrEt]^+ + C_2H_4$. Stationary points corresponding to four β-agostic complexes $[(1,2\text{-}Me_2Cp)_2Zr(Et)C_2H_4]^+$ (**7a—d**), which differ in the mutual arrangement of the Me groups, were located on the potential energy surface of the $[(1,2\text{-}Me_2Cp)_2ZrEt]^+ + C_2H_4$ system. The structures of the agostic complexes are shown in Fig. 3. The relative energies are 0, 0.47, 1.24, and 1.72 kcal mol^{-1} for **7a**, **7b**, **7c**, and **7d**, respectively. The arrangement of the substituents in conformer **7a** corresponds to that observed in the crystal structure of $(1,2\text{-}Me_2Cp)_2ZrMe^+MeB(C_6F_5)_3$ studied previously.[13] In the structure of conformer **7b**, the methyl substituents are located at maximum possible distances both from each other and from the atoms of the ethyl fragment and the ethylene molecule. Other conformers (**7c** and **7d**) are characterized by noticeably higher energies and are not considered from here on.

Of two possible transition states **8a** and **8b** (see Fig. 3, *e*—*f*) appearing in the course of isomerization of β-agostic complex **7** into the corresponding α-agostic complex, state **8a** is characterized by lower values of the energy E (Table 5), ΔH_0, and the free energy ΔG_{298}. Hence, state **8a** should be considered as a transition state of the key stage of chain propagation. Then, the activation energy of this stage is 4.4 (3.8 for R = Me) kcal mol^{-1} and ΔG_{298} = 4.2 (3.6—3.3 for R = Me) kcal mol^{-1}.

Structures and energies of intermediates and transition states of the reaction $[(Me_4Cp)_2ZrEt]^+ + C_2H_4$. The structures of adduct **7** formed by $[(Me_4Cp)_2ZrEt]^+$ with an ethylene molecule and transition state **8** of the rate-

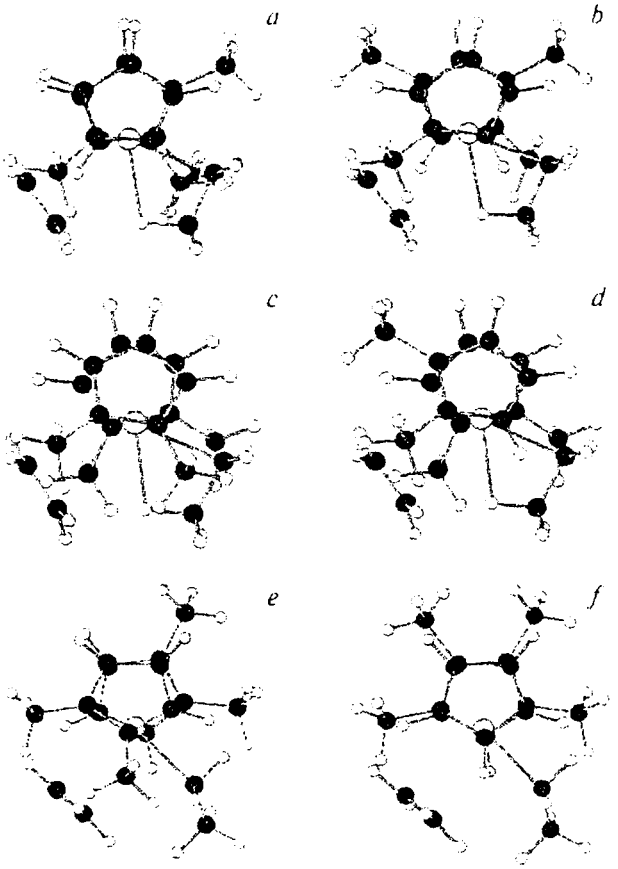


Fig. 3. Structures of the complexes $[(1,2\text{-}Me_2Cp)_2Zr(C_2H_4)Et]^+$ and the corresponding transition states of their isomerization: **7a** (*a*), **7b** (*b*), **7c** (*c*), **7d** (*d*), **8a** (*e*), and **8b** (*f*).

Table 5. Energies and thermodynamic parameters of the conformers of β-agostic complexes **7**, $[(Me_nCp)_2Zr(Et)C_2H_4]^+$ (n = 2 or 4), and transition states **8** of the chain-propagation reaction

Compound	n	ν_{imag} /cm^{-1}	ΔE	ΔH_0	ΔH_{298}	ΔG_{298}	ΔS_{298} /cal mol^{-1} K^{-1}
			kcal mol^{-1}				
7b		–	0.47	0.53	0.49	1.20	−2.39
8a	2	147i	5.50	4.39	4.49	4.23	0.87
8b		151i	6.09	5.28	5.20	6.02	−2.75
8	4	88i	3.78	3.60	3.29	4.39	−3.67

Note. The parameters are given relative to conformer **7a**, for which all values presented in the table are taken as zero.

determining reaction stage were optimized. The energy and thermodynamic characteristics of these structures are given in Table 5. For the key stage of the reaction, ΔH_0 = 3.6 kcal mol^{-1}, which is noticeably smaller than that in the case of R = 1,2-Me_2 (4.4 kcal mol^{-1}) and is approximately equal to that in the case of R = Me (3.8 kcal mol^{-1}); the free activation energy ΔG_{298} = 4.4 kcal mol^{-1} (4.2 and 3.6–3.3 kcal mol^{-1} for R = 1,2-Me_2 and R = Me, respectively).

The rate constant of a monomolecular reaction is proportional to $\exp(-\Delta G^{\neq}/RT)$ and, consequently, the dependence of $\Delta G^{\neq}$ on ln k should be linear.[12] The dependence of the $\Delta G^{\neq}_{326}$ values (for **8a**–**e** and **7a**), which were calculated in the present work for the stage of isomerization of β-agostic complex **7** into the corresponding α-agostic complex, on the logarithm of the experimental rate constant of chain propagation measured previously[8] is shown in Fig. 4. The theoretical values presented in Fig. 4 were calculated at 326 K (the temperature at which the rate constants were experimentally measured). The logarithm of the experimental rate constant of chain propagation increases in the series H–Me–1,2-Me_2–Me_4–Pr^n–Bu^n. It can be seen from Fig. 4 that the $\Delta G^{\neq}_{326}$ values calculated for the series of dialkyl-substituted zirconocenes (R = Me, Pr^n, or Bu^n) linearly depend on the experimentally measured rate constants of chain propagation. However, the calculated parameters for polymethyl-substituted zirconocenes (R = 1,2-Me_2 or Me_4) noticeably deviate from this dependence. For the polymethyl-substituted zirconocenes, the ΔG_{326} values are substantially higher than the corresponding values for all other catalysts under consideration, including unsubstituted zirconocene (R = Cp). This signifies that the rate constants of chain propagation for these two zirconocenes should be smaller than those for the remaining compounds. Nevertheless, these zirconocenes are intermediates between the compounds with R = Me and Pr^n (see Fig. 4).

Therefore, there is no correlation between the calculated and experimental parameters in the case of polyalkyl-substituted zirconocenes (R = 1,2-Me_2 or Me_4). Apparently, this indicates that the kinetics of the process is controlled also by factors other than the energy of isomerization of β-agostic complex **7** into the

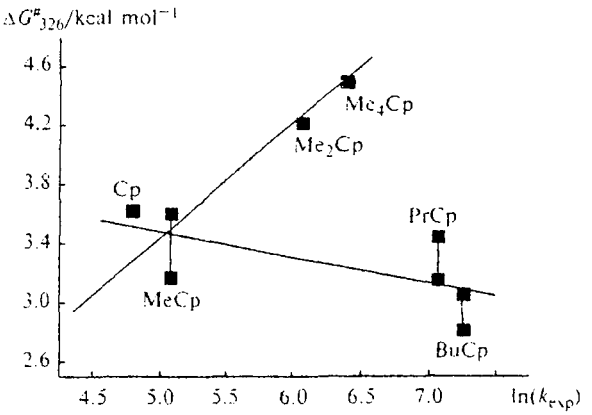


Fig. 4. Dependence of the calculated $\Delta G^{\neq}_{326}$ values on the logarithm of the experimental rate constants of chain propagation.

corresponding α-agostic complex through transition state **8**. To account for the results obtained, we attempted to estimate the effects (of the direction and extent) of other stages on the kinetics of the process.

Reaction of the catalysts with the MeMAO$^-$ counterion

To elucidate the effect of reaction (1) on the kinetics of chain propagation, let us consider the simplest model (4) for reaction (1):

$$(RCp)_2Zr(Et)Me\ (\mathbf{9}) + C_2H_4 \rightleftharpoons$$

$$\rightleftharpoons [(RCp)_2Zr(Et)C_2H_4]^+\ (\mathbf{7a}) + Me^- \qquad (4)$$

This reaction describes equilibrium between β-agostic adduct **7a**, which is directly involved in the key stage of the reaction, and the latent state of catalyst **9**. The energies and the standard thermodynamic characteristics of reaction (4) are given in Table 6. The dependence of the calculated $\Delta\Delta G_{326}$ values for reaction (4) on the experimental parameters (T = 326 K) is shown in Fig. 5. The $\Delta\Delta G_{326}$ values are equal to ΔG_{326} on condition that ΔG_{326} for the compound with R = Me_4 is taken as zero. It can be seen from Fig. 5 that the dependence of $\Delta\Delta G_{326}$ on ln k in the series of zirconocenes with R = H, Me, Pr^n, and Bu^n is to a first approximation linear. The $\Delta\Delta G_{326}$ value decreases in the series of the compounds under consideration, *i.e.*, the addition of the ethylene molecule giving rise to a separated ion pair is thermodynamically more favorable for the substituents containing a large number of C atoms, which, in turn, should lead to an increase in the experimental effective rate constant of chain propagation. It is the contribution of this stage to the overall kinetics of the process that may be responsible for the stronger dependence of the experimental rate constants on the length of the hydrocarbon substituent in the cyclopentadienyl ring compared to the dependence of the rate constants calculated from ΔG_{298} of activation.

In the case of polymethyl-substituted zirconocenes, the dependence deviates from linearity. The data shown

Table 6. Energies and thermodynamic parameters for model reaction (4) with the cocatalyst

Parameter	H	Me	Pr^n	Bu^n	1,2-Me_2	Me_4
ΔE/kcal mol^{-1}	173.03	170.15	168.63	168.22	169.08	167.04
ΔH_0/kcal mol^{-1}	171.75	168.56	167.18	166.88	167.55	165.69
ΔH_{298}/kcal mol^{-1}	171.93	168.88	167.43	167.09	167.84	165.86
ΔS_{298}/cal mol^{-1} K^{-1}	−3.05	−3.54	−4.26	−4.71	−1.87	−5.49
ΔG_{298}/kcal mol^{-1}	172.84	169.94	168.70	168.50	168.40	167.50

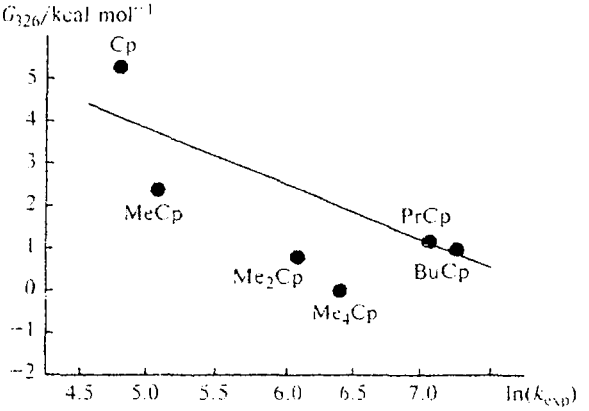


Fig. 5. Dependence of the calculated ΔG_{326} values for model reaction (3) on the logarithm of the experimental rate constants of chain propagation. For $[(Me_4Cp)_2Zr(C_2H_4)Et]^+$, the calculated ΔG_{326} value is taken as zero.

in Fig. 5 indicate that the addition of ethylene to these compounds and the formation of separated ion pairs should proceed more readily than those in the case of all other zirconocenes under consideration and, correspondingly, the experimental effective rate constants are higher than those calculated from the ΔG values. These differences are responsible for the discrepancy between the experimental and calculated rate constants of chain propagation. From this it follows that stage (1) contributes significantly to the kinetics of the process.

In the present work, the mechanism of the reaction of the substituted ethylzirconocene cations $(RCp)_2ZrEt^+$ with an ethylene molecule is analyzed in detail for the first time. This made it possible to compare the results of calculations with the experimental data on rate constants of chain propagation.

The use of the model of an *isolated cation*, which does not take into account interactions with the $MeMAO^-$ counterion, allows one to obtain only the qualitative correspondence between the calculated and measured kinetic characteristics in the simplest homologous series of dialkyl-substituted catalysts (R = H, Me, Pr^n, or Bu^n). The quantitative examination as well as the extension of the range of zirconocenes under consideration by including the polyalkyl-substituted compounds (R = 1,2-Me_2 or Me_4) led to the absence of the correlation between the calculated and experimental characteristics.

To account for the results obtained in this work, the simplest model reaction (3) of the replacement of the $MeMAO^-$ counterion by an ethylene molecule followed by the displacement of the former to the outer coordination sphere about the Zr atom was considered. Both stages of the process, *viz.*, (1) and (2), were demonstrated to make comparable contributions to the kinetics of the process under study. Unlike the *isolated cation* model, the *ionic pair* model[14,15] allows one to study interaction with the counterion.

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