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The quantum-chemical analysis of mechanism of radical-initiated polymerization of styrene in the presence of ferrocene

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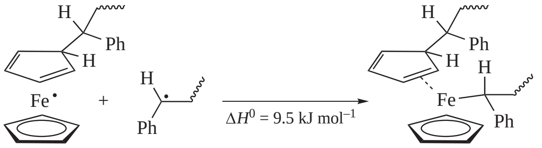
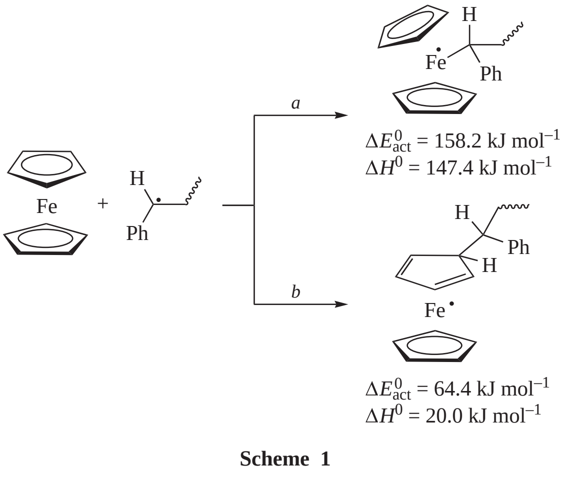
The transformations occurring in the course of radical-initiated polymerization of styrene in the presence of ferrocene have been analyzed using TPSSTPSS/TZVP method of the density functional theory.



The principle of controlled/living radical polymerization is introduction in the polymerization system of special agents which temporarily bind propagating radicals in so-called ‘dormant’ form, which results in significant suppression of termination reactions.[1–9] When metal complexes are used as such agents, the metal–carbon bonds are formed in the arrangement of ‘dormant’ chains.[1,2] The chain propagation reaction in the ion coordination polymerization occurs *via* insertion of the monomer molecules into metal–carbon bonds. In case of the controlled/living radical polymerization, the possibility of such an insertion (*i.e.* coordination chain propagation reaction) has not been discussed so far. However, some experimental facts indirectly indicate such a possibility. For example, radical-initiated polymerization in the presence of metallocenes has controlled/living character since the polymers obtained show linear increase in average molecular weight on growth of the monomer conversion; moreover, these polymers are capable of initiating polymerization of a new portion of monomer.[10–12] These polymers have bimodal molecular weight distributions[10–12] as indicated by two types of chain propagation sites. Accordingly, it becomes valuable to analyze the feasibility of realization of controlled/living radical mechanism and to study coordination chain propagation reaction by quantum chemical methods to compare with the experimental facts. The herein research object is radical-initiated polymerization of styrene in the presence of ferrocene. The relevance of this study is conditioned by the need of knowing the mechanisms of polymerization, which is important for both fundamental science and polymer industry. Since the possibilities of experimental studying the mechanisms of elementary acts occurring in complex systems are very limited, the methods of quantum-chemical modeling are actively used.[13–15]

When considering the interaction of a simulating styrene propagating radical ($\mathrm{MeCH_2^{\bullet}CHPh}$) (Scheme 1) with $\mathrm{Cp_2Fe}$, it was established that this radical can be attached to the Fe atom (reaction *a*), and to the cyclopentadienyl ring (reaction *b*).†



Scheme 1

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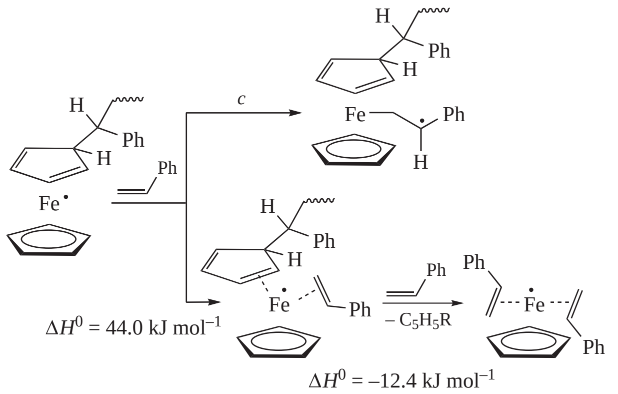
† The quantum chemical calculations were carried out in Gaussian’09[16] using TPSSTPSS/TZVP method.[17,18] The type of the stationary point on the potential energy surface was determined based on Hessian matrix calculations. The thermal effects (ΔH^0) and the activation barriers ($\Delta H^0_{\mathrm{act}}$) were calculated by Hess’s law at 298 K. In case of metal-containing structures which can exist in different spin states (singlet or triplet, doublet or quartet), for ΔH^0 and $\Delta H^0_{\mathrm{act}}$ calculations, energetically more favorable states were used.

The search for transient states was carried out by the method of relaxation scanning of the potential energy surface (PES) along the reaction coordinate, for which two corresponding atoms were chosen and the distance between them was reduced (from 4 to 1.3 Å). The resulting cut of the PES profile was analyzed for the case of existence of a maximum corresponding to the transition state of the reaction. The structure corresponding to the maximum was processed towards optimizing the transition state without limiting the number of negative eigenvalues. The Hesse matrix was calculated for the optimized structure of the transition state. The presence of one imaginary frequency was a confirmation of the accuracy of the solution.

The adequacy of the used quantum-chemical method is confirmed by a good correspondence of the calculated structural and energy characteristics of the objects of the system in question. Thus, the interatomic distances in the ferrocene molecule (the values were calculated by the TPSSTPSS/TZVP method / experimentally found value[19]) are: Fe–C, 2.047/2.05 Å; C–C, 1.434/1.43 Å; C–H, 1.082/1.11 Å. The activation barrier of free-radical propagation reaction of polystyrene chain (calculated by the used method) estimated as the difference between the absolute enthalpy of the transition state and the initial particles was 26.7 kJ mol^{-1} (in the case of the activation barrier in the form of E_{act}, *i.e.* using the graph of the reaction rate constant *versus* the reciprocal temperature, this value was 32.1 kJ mol^{-1}), whereas the experimentally determined value was 30.3 kJ mol^{-1}.[20]

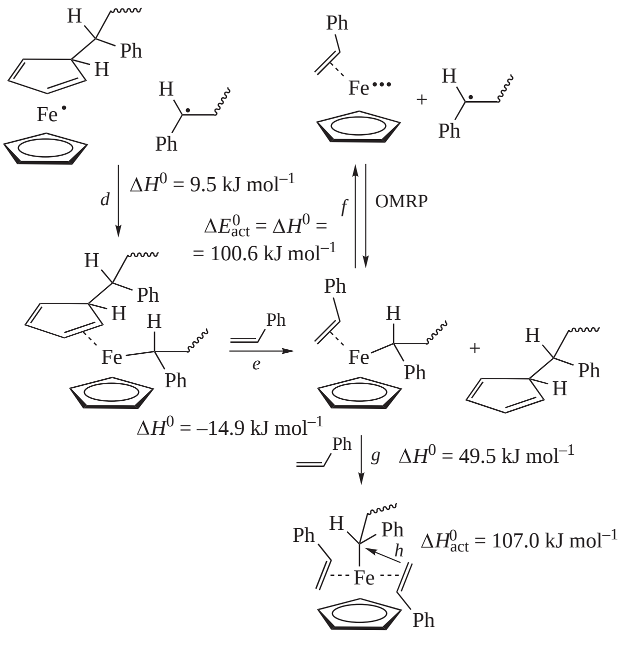
Reaction *a* corresponds to organometallic mediated radical polymerization (OMRP) mechanism of controlled/living radical polymerization[1,2] but it is less likely, $\Delta H^0_{\text{act}} = 158.2$ kJ mol^{-1}. Attachment of R$^{\bullet}$ to the cyclopentadienyl ring has a higher probability. As a result for reaction *b*, an intermediate CpFe$^{\bullet}$(C$_5$H$_5$R) is formed. This compound cannot initiate a chain propagation (Scheme 2, reaction *c*), because the points corresponding to the attached product do not exist on the curve of potential energy surface. In principle, the reaction of cyclic diene C$_5$H$_5$R ligand exchange with two molecules of styrene is possible. This process, as shown in Scheme 2, occurs in two stages.



Scheme 2

The intermediate CpFe$^{\bullet}$(C$_5$H$_5$R) can potentially act as a spin trap and regulate the process according to the OMRP (Scheme 3, reaction *d*).

The adduct CpFeR(C$_5$H$_5$R) is capable of coordinating interaction with monomer (Scheme 3, reaction *e*). Hereby a displacement of the substituted cyclopentadienyl ligand proceeds from the coordination sphere of the Fe atom. Monomer molecule is coordinated by its double bond to the Fe atom, and the product of this reaction is a complex CpFe(styrene)(R). The process of the propagating radical release from such complex with CpFe$^{\bullet\bullet\bullet}$(styrene) spin trap regeneration (reaction *f*) is rather energy consumptive, $\Delta H^0_{\text{act}} = 100.6$ kJ mol^{-1}. This indicates a high efficiency of intermediate CpFe$^{\bullet\bullet\bullet}$(styrene) as a spin trap, because the reverse reaction is an attachment of R$^{\bullet}$ by metal atom to CpFe$^{\bullet\bullet\bullet}$(styrene) occurring with the energy release of 100.6 kJ mol^{-1}.

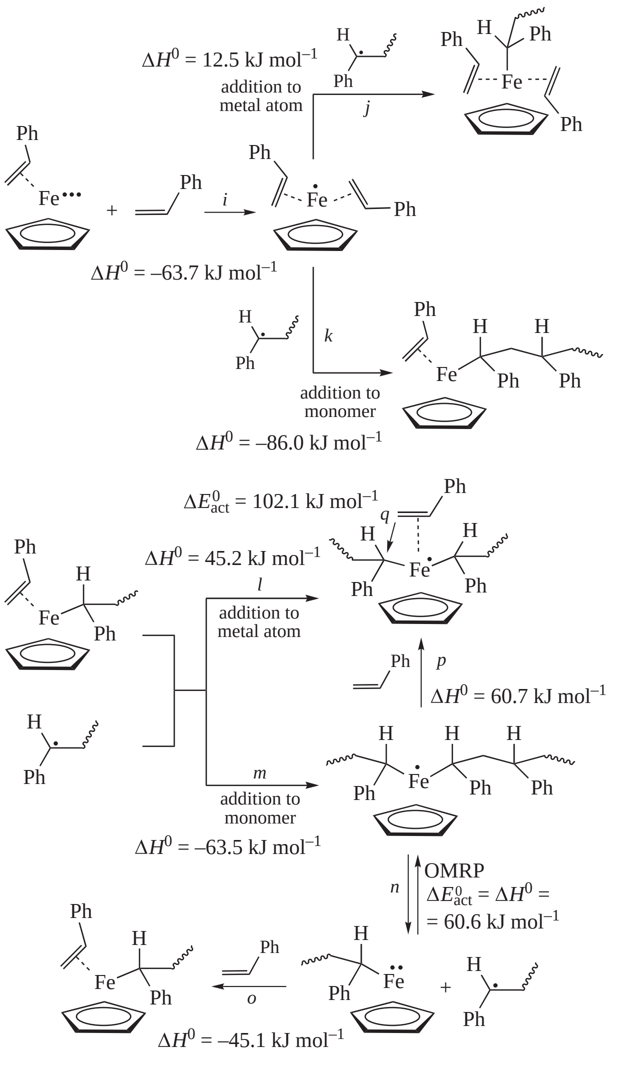


Scheme 3

During the interaction of CpFe(styrene)(R) intermediate with a styrene molecule (reaction *g*), the chain propagation can proceed to form CpFe(styrene)$_2$(R) complex by a similar ion coordination olefins polymerization mechanism (reaction *h*).

The chain propagation reaction in CpFe(styrene)(R) complex has $\Delta H^0_{\text{act}} = 146.0$ kJ mol^{-1}, *i.e.* this process is much less likely compared to the chain propagation in CpFe(styrene)$_2$(R) active site.

The CpFe$^{\bullet\bullet\bullet}$(styrene) intermediate formed *via* reaction *f* (see Scheme 3) will be inevitably solvated by the monomer (Scheme 4, reaction *i*) thus leading to species CpFe$^{\bullet}$(styrene)$_2$. The latter can attach a radical by the Fe atom (reaction *j*), but due to steric hindrances, such a process should occur with low energy absorption. Reaction *k* seems more likely.



Scheme 4

The intermediate CpFe(styrene)(R) is ineffective as a spin trap because the energy absorption of the propagating radical attachment is 45.2 kJ mol^{-1} (reaction *l*). However, radical may attach to the styrene molecule coordinated in CpFe(styrene)(R) complex. This reaction with the energy release of 63.5 kJ mol^{-1} leads to species CpFe(R)$_2$ (reaction *m*) and is characterized by $\Delta H^0_{\text{act}} = 46.0$ kJ mol^{-1}. Compared to a free-radical chain propagation reaction ($\Delta H^0_{\text{act}} = 30.3$ kJ mol^{-1}),[20] the running of such chain propagation reaction is more difficult.

The CpFe(R)$_2$ intermediate formed *via* reaction *l* can participate in OMRP (reaction *n*), wherein the polymer chain binding strength in it is smaller than that in CpFe(styrene)(R) structure, and therefore this equilibrium can provide a polymerization in controlled/living mode at lower temperatures (as compared to equilibrium *f*, see Scheme 3). Its further interaction with the monomer (reaction *o*) again leads to species CpFe(styrene)(R).

The coordination chain propagation may also occur in CpFe(R)_2(styrene) complex (reaction *q*, $\Delta H^0_{\text{act}} = 102.1$ kJ mol^{-1}) formed by reactions *l* and *p*.

Thus, the following conclusions can be made based on the herein performed quantum-chemical analysis. (1) The primary channel for the formation of macromolecules should be a free-radical chain propagation reaction. (2) Further $\text{CpFe}^\bullet(\text{C}_5\text{H}_5\text{R})$ radical conversions including monomer molecules and propagating radicals lead to the formation of intermediates which can participate both in OMRP and in coordination chain propagation reactions. (3) The capability of polystyrene to initiate polymerization of new monomer portions is caused by the presence of ‘dormant’ chains, CpFe(styrene)(R) and CpFe(R)_2. The bimodal molecular weight distribution of the polystyrene is bespoken by the presence of coordination active sites along with the propagating radicals.

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