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Compensation Effect in Polymerization Kinetics on Homogeneous Catalysts

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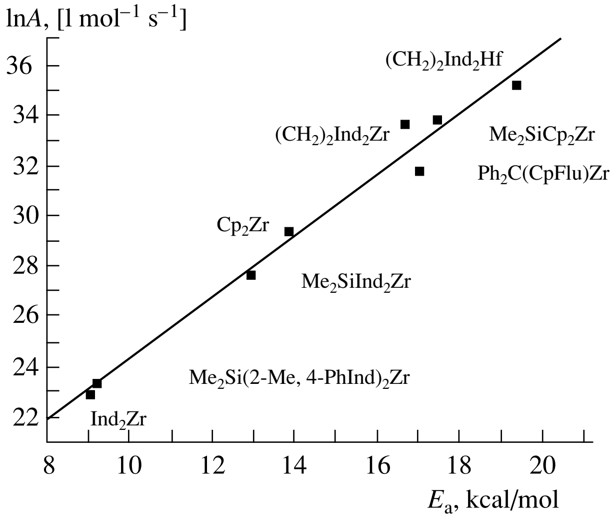
Olefin polymerization in the presence of homogeneous catalysts is one of the most important branches of chemistry [1–7]. Recently, systematic studies [1, 6–8] of new highly active catalysts based on (semi)sandwich complexes of IVB group metals and new-type cocatalysts—polymethylalumoxane (MAO), perfluorophenylboranes, and perfluorophenylborates—have been carried out [6]. In this work, we used these systems and for the first time demonstrated for Ziegler–Natta catalysts the existence of the relationship between the preexponential factors A and the activation energies E_a in the Arrhenius equation for the rate constants of polymerization.

When analyzing the rate constants [7, 8] of polymerization of ethylene in toluene with zirconocene and hafnocene complexes $(\pi\text{-L})_2MCl_2$ activated with MAO in the range 10–90°C we found that depending on the nature of ligand environment and the transition metal ion, the experimental values of $\ln A$ and E_a drastically range (E_a varies between 9 and 20 kcal/mol and $\ln A$ varies between 23 and 35 l mol^{-1} s^{-1}). The temperature dependences of the initial rates of the reaction are described well by the Arrhenius equation [7, 8]. Theoretically [3, 1], the step of ethylene insertion into a M–C_α bond in the free cationic active center [2] occurs with almost zero activation energy, whereas the energies of reorganization of various ion pairs [metallocene (Zr, Hf) + cocatalyst] known from the literature (NMR data [1]) range from 10 to 20 kcal/mol in the absence of an olefin. The same values of activation energies (see figure) are observed under real conditions of a catalytic process. It is reasonable to assume that the observed compensation effect (see figure) is thermodynamic in this case and corresponds to the cymbate linear dependence between the entropy of activation and the heat of dissociation of precatalytic ion pairs into free counterions. The isokinetic temperature (142°C) is noticeably outside the temperature interval where the rate constants were measured (10–90°C) and thus the compensation effect is most likely true and is not associated with error in the measurements of temperature dependences of the ethylene polymerization rate constants.

Thus, there is a linear relationship between $\ln A$ and E_a, which is fulfilled well for various systems based on zirconium and hafnium. The fact that points belonging to different complexes fall on the same straight line suggests that the mechanism of action of active centers for polymerization and the ionic nature of the transition state of the reaction center in the key step of the catalytic process are the same. The existence of the compensation effect suggests that, in the case of more active catalysts (characterized by lower activation energies), the solvation of active ionic forms (or ion pairs) is enhanced simultaneously, and the molecules of the substrate and a cocatalyst probably participate in this process (the inflexibility becomes more pronounced: the number of internal rotations decreases).

Note that, despite many contributions in this field, the compensation effect is probably observed for the first time. We hope that a further study of this effect will let us draw more certain conclusions on the mechanism of this important catalytic process.



Compensation dependence between the parameters $\ln A$ and E_a in ethylene polymerization with metallocene complexes activated by polymethylalumoxane. The conditions for polymerization [7, 8]: [M] = const = 1×10^{-5} mol/l, $[Al_{MAO}]$ = const, $[Al_{MAO}]/[M]$ = 3000 mol/mol; the order of formation of the catalyst was the same in all cases.

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