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Reaction of Metallocenes with Maleic Anhydride

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Abstract—Spectral investigation applying UV, IR, and ^{1}H NMR techniques to the reaction of ferrocene, titano- and zirconocene dichlorides with maleic anhydride was carried out. It was found that in all cases charge transfer complexes were formed. It was showed that the structure of the metallocene affected both the process of the formation and structure of the complexes.

Keywords: maleic anhydride, ferrocene, titanocene dichloride, zirconocene dichloride, coordination complex formation, charge transfer complex

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Metallocenes are attractive for the investigators in the field of organic and polymeric synthesis; they have been actively studied as the components of initiating systems for coordination radical polymerization [1, 2]. It has been found that the influence of metallocenes of various metals on the process of polymerization was different. Thus, ferrocene significantly accelerated polymerization of vinyl monomers especially if peroxide compound was used as an initiator (for example, benzoyl peroxide) [2, 3]. In this case besides the rate increase, the activation energy of polymerization is fairly reduced which is important in the technological respect. On the other hand, the ferrocene presence has an impact on polymer properties, namely, the molecular mass pronouncedly reduces but the polydispersity practically does not change; polymer thermal stability increases together with the content of sequences of the syndio-structure (up to ~85%) [3, 4].

Unlike ferrocene, titanocene and zirconocene dichlorides have different influence on the polymerization process: rate increase and reducing the average degree of polymerization are significantly less than in the case of ferrocene, but the activation energy is considerably lower in their presence [5, 6]. The experimental data show that the compounds of titanium and zirconium transfer the process more strongly into the mode of coordination radical polymerization [7].

The behavior of metallocenes in the process of radical copolymerization has been poorly investigated. Yet quite a number of large-capacity copolymers have been prepared based on maleic anhydride. However, the activity of maleic anhydride in polymerization processes is rather low [8]. The use of pseudo-living and coordination radical polymerization based on introduction of special additives into the polymerization system is one of the approaches to the solution of the problem.

Taking into consideration an importance of maleic anhydride copolymers and its ability to participate in the complex formation processes we performed the investigation of the reaction of maleic anhydride with ferrocene Cp_2Fe, titanocene Cp_2TiCl_2, and zirconocene Cp_2ZrCl_2 dichlorides.

The complex formation process can be monitored, in particular, by UV spectroscopy. After mixing the solutions of maleic anhydride with Cp_2Fe, in the UV spectrum a peak with λ_{max} = 622 nm appeared, the solution got green, and the absorption of maleic anhydride in the spectrum almost disappeared (Fig. 1). Ferrocene absorbs light at λ_{max} = 439 and 325 nm and has no absorption bands in the region of $\lambda > 550$ nm; maleic anhydride absorbs light at λ_{max} = 750 nm and almost does not absorb in the region from 500 to 700 nm.

In the ^{1}H NMR spectra of the mixture of ferrocene with maleic anhydride some changes were also observed (Fig. 2). The signal of the protons of cyclopentadienyl rings of ferrocene (4.07 ppm) was

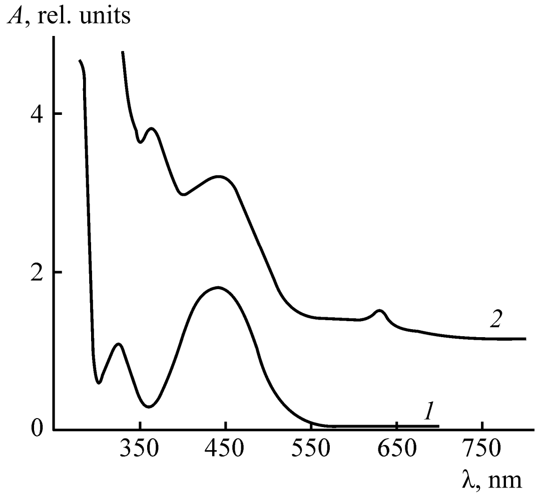


Fig. 1. UV spectra of ferrocene (*1*), and its equimolar mixture with maleic anhydride (*2*) at 20°C in methanol.

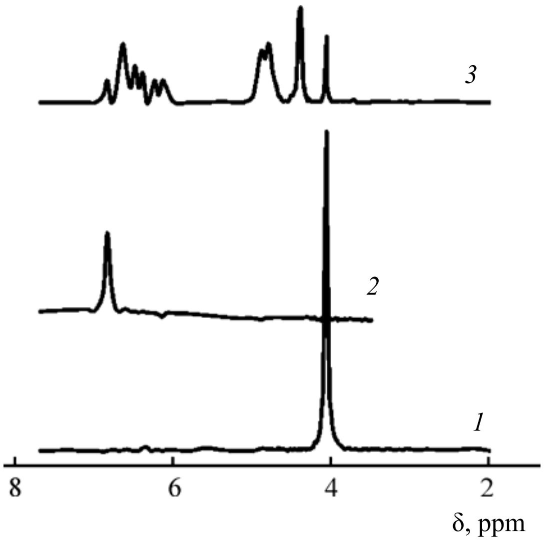


Fig. 2. ^{1}H NMR spectra of ferrocene (*1*), maleic anhydride (*2*), and their equimolar mixture (*3*) in $CDCl_3$ at 20°C.

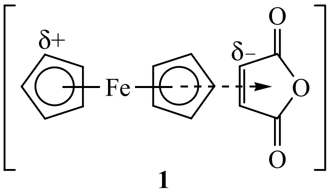
reduced in intensity and two new signals at 4.40 ppm and in the region 4.60–5.00 ppm appeared. This might be due to the loss of the symmetry of the molecule and indicated the preferential involvement of one of the cyclopentadienyl rings into the reaction.

The formation of the complex was also confirmed by the character of the change in the signal of protons of maleic anhydride (Fig. 2): multiplet signal in the region 6.10–6.90 ppm appeared instead of the singlet at 6.85 ppm.

It should be noted that the signals of protons of ferrocene (4.07 ppm) and maleic anhydride (6.85 ppm), which did not participate in the coordination complex formation were also present in the spectrum of the mixture. Most probably, the complex formation at investigated temperature (20°C) was reversible and did not entirely complete.

The character of the spectra change of the mixture of ferrocene and maleic anhydride evidenced the donor–acceptor interaction between them; ferrocene was a donor, and maleic anhydride an acceptor of electrons. It has been known [9] that ferrocene can participate in donor–acceptor interactions playing a role of active electron donor. Yet maleic anhydride more often displays acceptor properties [8]. Therefore in the first stage of the reaction most probably the formation occurred of donor–acceptor complex **1** (Scheme 1).

Scheme 1.



1

In the molecule of maleic anhydride there are both double bond C=C and carbonyl groups which are conjugated. According to the data of quantum chemical calculations of the reaction of ferrocene with such carbonyl-containing compounds as benzoyl peroxide and methyl methacrylate [10] a complex formation actively proceeds by the interaction of the carbonyl group with the iron atom of ferrocene; the coordination of C=C bond is less pronounced, however it can also occur. Besides it has been known [11] that the complex formation of ferrocene with methyl methacrylate (as distinct from benzoyl peroxide) requires more energy expenditure and has not been reliably detected. Obviously, the presence of two carbonyl groups in the molecule of maleic anhydride provides a possibility of detection of its complex with ferrocene by spectral methods.

Spectral investigation of the reaction of titanocene and zirconocene dichlorides with maleic anhydride showed that it differed substantially from the process with ferrocene.

Thus, titanocene dichloride Cp_2TiCl_2 did not absorb at $\lambda > 380$ nm, and the maximum of absorption was with $\lambda_{max} = 262$ nm. After mixing its solution with a

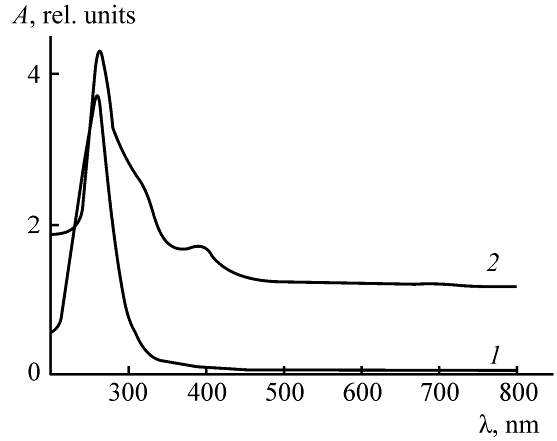


Fig. 3. UV spectra of solution of titanocene dichloride (1×10^{-4} mol/L) (*1*) and its equimolar mixture with maleic anhydride (*2*) in chloroform at 20°C.

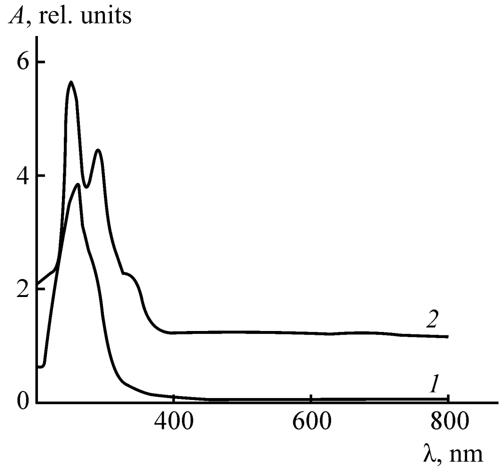


Fig. 4. UV spectra of solution of zirconocene dichloride (1×10^{-4} mol/L) (*1*) and its equimolar mixture with maleic anhydride (*2*) in chloroform at 20°C.

solution of maleic anhydride a new absorption peak with λ_{max} = 390 nm appeared in the spectrum that evidenced their reaction with each other and the formation of the complex (Fig. 3).

In the case of zirconocene dichloride Cp_2ZrCl_2 the absorption at $\lambda > 350$ nm was absent and the maximum of absorption was observed at λ_{max} = 260 nm. After addition of maleic anhydride this peak was shifted in the region of larger energies (up to 256 nm), and in the spectrum new peak at λ_{max} = 290 nm arose and the absorption in the region of $\lambda_{max} \approx 350$ nm increased (Fig. 4). Therefore the changes in the UV spectrum also confirmed the reaction of zirconocene dichloride with maleic anhydride.

The process of complex formation in the case of compounds of Ti and Zr proceeded in a different way than with ferrocene. Additional information about the nature of the reaction can be obtained based on IR spectral investigation. Thus, in the IR spectrum of the mixture of titanocene with maleic anhydride an absorp-

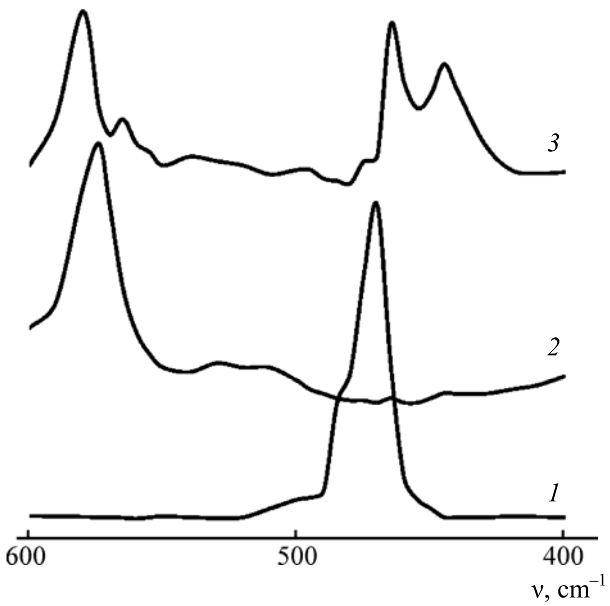


Fig. 5. IR spectra of solutions of titanocene dichloride (1×10^{-2} mol/L) (*1*), maleic anhydride (*2*), and their equimolar mixture (5×10^{-4} mol/L each) (*3*) in benzene at 20°C.

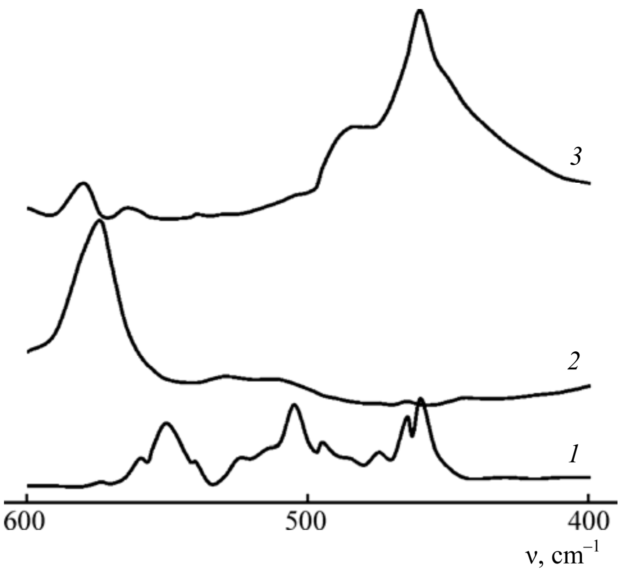
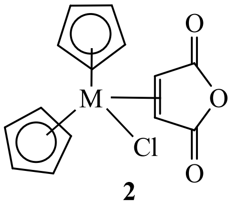


Fig. 6. IR spectra of solutions of zirconocene dichloride (1×10^{-2} mol/L) (*1*), maleic anhydride (*2*), and their equimolar mixture (5×10^{-4} mol/L each) (*3*) in benzene at 20°C.

Scheme 2.



2

M = Ti; Zr.

tion band at 470 cm^{-1} was observed, which corresponded to the stretching vibrations of the bond metal–aromatic ring. This band after addition of monomer was shifter by 6 cm^{-1} (Fig. 5), and a new peak at 444 cm^{-1} appeared that was most probably evidenced the loss of relative symmetry of the molecule of titanocene dichloride in the course of its reaction with maleic anhydride. Interestingly, the location of the signal of carbonyl group of the anhydride was also changed: it suffered a blue shift by 6 cm^{-1}.

Similarly in the spectrum of the mixture of solutions of zirconocene dichloride and maleic anhydride a shift and a change in the appearance of the absorption bands of cyclopentadienyl rings with maxima at 464 and 504 cm^{-1} were observed (Fig. 6).

Based on the study of the reaction of zirconocene dichloride with methyl methacrylate containing both ester functionality and conjugated double bond in the molecule we suggested [11] that the coordination bond formed between zirconium atom and the oxygen of the carbonyl group. However, the coordination of the molecule of maleic anhydride at the metal atom as a result of chlorine atom exchange that is typical for metallocenes dichlorides [12] cannot be excluded completely. Taking into account the conjugation of the bonds in maleic anhydride molecule the formation of the coordination complex **2** is the most probable for Cp_2TiCl_2 and Cp_2ZrCl_2 (Scheme 2).

In summary, the investigated metallocenes reacted readily with maleic anhydride; the specific features of their interaction were caused by the structure of organometallic compound.

EXPERIMENTAL

Maleic anhydride was twice distilled in a vacuum before use, bp = 52.85°C (30 mmHg), d_4^{20} = 1.48 g/mL. Metallocenes of pure grade (from Aldrich) were used. Solvents were purified according to the known procedures [13].

IR spectra were recorded on a FSN 1201 Monitoring Fourier spectrometer. UV spectra were registered on a Shimadzu UV-2450 instrument. ^{1}H NMR spectra were obtained on a spectrometer AM-300 Bruker at 300 MHz using $CDCl_3$ as a solvent and tetramethylsilane as a reference.

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