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NATURE OF THE DONOR-ACCEPTOR REACTION OF MALEIC  
ANHYDRIDE WITH THE VINYL ETHER OF BENZYL ALCOHOL

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In studying complexing and copolymerization of maleic anhydride (MA) with butyl vinyl (BVE) and phenyl vinyl (PVE) ethers, it was hypothesized [1, 2] that if overlapping of the orbitals of the double bonds in the monomers occurs in the donor-acceptor (DA) reaction, a significant increase is observed in their reactivity; with sufficiently high concentrations of the complex, the copolymerization reaction will take place almost solely by the addition of these monomeric complexes to the propagating macroradical. If the  $\pi$  orbital of the double bond in MA overlaps the  $\pi$  orbital of the fragment of the comonomer molecule not involved in polymerization, a decrease should be observed in the reactivity of this monomer in the copolymerization reaction.

The DA reaction of MA with the vinyl ether of benzyl alcohol (VEBA) was studied to investigate the effect of the electronic structure of the complexes on the reactivity of the monomers and the mechanism of alternating copolymerization.

EXPERIMENTAL

The complexing study was conducted with a Specord UV-Vis spectrometer. The equilibrium constants ( $K_e$ ) of the complexes of VEBA and ethylbenzene (EB) with MA were determined as in [3] for solutions in cyclohexane. The concentration of the ethers varied from 1.5 to 5.7 moles/liter with a constant concentration of MA (0.05 mole/liter). The thickness of the absorbing layer was varied from 0.05 to 0.02 cm. The experimental data were processed by the method of least squares with a regression analysis program.

The quantum-chemical calculations for VEBA were performed for the conformation in which the plane of the benzene ring coincides with the plane of the vinyloxy group (form (IV), see below).

The  $^{13}\text{C}$  NMR spectra were recorded on a Varian XL-100/12 spectrometer at  $25 \pm 0.1^\circ\text{C}$ . Fixed concentrations of the donor in cyclohexane with variable concentrations of MA were used for recording the NMR spectra. The solvent was the internal standard. The precision of measurement of the  $^{13}\text{C}$  chemical shifts (CSs) was  $\pm 0.01$  ppm.

The dielectric constants were measured on an Epsilon instrument (1 MHz) at  $25 \pm 0.1^\circ\text{C}$ . The concentration of VEBA in cyclohexane varied from 0 to 0.07485 mole/liter with a constant concentration of MA (0.02926 mole/liter).

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TABLE 1. Constants of Complexing of the Vinyl Ether of Benzyl Alcohol and Ethylbenzene with Maleic Anhydride

Donor	$\lambda_{\max}$ , nm	$K_e$ , liter/mole	$\epsilon_{DA}$ , liter/mole·cm	$r$	$s_0$
VEBA	275	0,43±0,02*	1340	0,999	0,0002
VEBA	275	0,45±0,06†	1390	0,995	0,0006
VEBA	275	0,46±0,08‡	1413	0,994	0,0007
EB	276	0,22±0,03	1627	0,982	0,0001

\*With the Ketelaay equation.

†With the Frank-Oswald equation.

‡With the Foster equation.

#### DISCUSSION OF RESULTS

An absorption band at 205 nm with extinction ( $\epsilon = 12,000$  liters/mole·cm), the sum of the superposition of two bands caused by  $\pi-\pi^*$  transitions in the benzene ring and the vinyloxy group, and bands at 258 nm ( $\epsilon = 196$ ) and 264 nm ( $\epsilon = 150$  liters/mole·cm), caused by  $\pi-\pi^*$  transitions in the benzene ring, are observed in the electron spectra of VEBA in cyclohexane; the UV spectra and the data in [4] indicate the absence of  $\pi-p-\pi$  conjugation in the molecule of this ether. In studying the absorption spectra of solutions of MA and VEBA in cyclohexane, an absorption band with  $\lambda_{\max} \approx 275$  nm was found. The appearance of this band is due to the formation of a DA complex of MA with VEBA, since in the concentrations used, the absorption of the starting components is low in this region and is well compensated with the use of a solution of the ether in cyclohexane with the same concentration in the comparison channel. The characteristics of the complexes are reported in Table 1. The values of  $K_e$  calculated with different equations are in good agreement.

In studying the nature of the DA reaction of MA with PVE, we previously [5] showed that charge transfer takes place with the highest occupied molecular orbital (HOMO) of the ether, to which all fragments of the molecule contribute due to  $\pi-p-\pi$  conjugation. The vinyloxy group and the benzene ring thus participate in complexing of PVE with MA.

There is no  $\pi-p-\pi$  interaction between the  $\pi$  systems of the phenyl and vinyloxy groups in the VEBA molecule due to the presence of a methylene bridge in the molecule. To determine which of the two fragments – the benzene ring or the vinyloxy group in VEBA – primarily participate in complexing with MA, quantum-chemical calculations for VEBA were performed, and the change in the chemical shifts ( $\delta$ ) in the  $^{13}\text{C}$  nuclei of the ether during complexing with MA was studied.

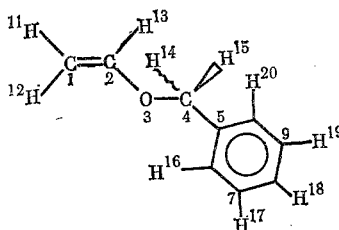
The ground state of the ether molecule was calculated by the CNDO/S method (the parameters in [6] and the geometry from [7] were used in the calculations). The energy of the molecular orbitals (MOs) and the contribution of the structural groups to the MO are reported in Table 2. As these data indicate, the three highest occupied orbitals (24, 25, 26) have a  $\pi$  nature and are similar in energy in the VEBA molecule.

Orbitals 24 and 26 are almost completely localized in the benzene ring, while MO 25 is located in the vinyloxy group with the predominant contribution of the vinyl group. The four lowest unoccupied orbitals (27, 28, 29, 30) are also  $\pi$  orbitals, and MOs 27, 28, and 30 are located in the benzene ring, while orbital 29 is in the vinyloxy group. As noted previously, in contrast to PVE, the MOs do not combine to form a single HOMO in the VEBA molecule, even in the case of the most favorable planar position of the  $\pi$  system of the benzene ring and the vinyloxy group, and this confirms the absence of  $\pi-p-\pi$  conjugation in the VEBA molecule.

The calculations performed indicate the possibility of charge transfer in complexing of MA with VEBA both from the benzene ring and from the vinyloxy group.

As a consequence, in the formation of a complex, each fragment of the ether molecule can be an independent  $\pi$  donor and the MA can enter the DA reaction either with the vinyloxy group alone or with the benzene ring or it can form a complex of the composition MA:VEBA = 2:1.

TABLE 2. Energy of the Molecular Orbitals and Contribution\* of the Structural Groups to the Molecular Orbitals of the Vinyl Ether of Benzyl Alcohol



No. of MO	$E_{MO}, eV$	Group			
		C=C	O	CH <sub>2</sub>	Ph
34	4.46				
33	4.24	0,053	0,007	0,190	0,751
32	4,08	0,007	0,004	0,275	0,715
31	3,51	0,002	0,003	0,103	0,892
30 $\pi$	2,43	0,0	0,0	0,005	0,995
29 $\pi$	0,41	0,955	0,043	0,002	0,0
28 $\pi$	0,03	0,001	0,0	0,0	0,999
27 $\pi$	-0,58	0,0	0,0	0,013	0,987
26 $\pi$	-9,26	0,031	0,019	0,057	0,893
25 $\pi$	-9,70	0,774	0,166	0,003	0,057
24 $\pi$	-10,33	0,0	0,0	0,003	0,997
23	-11,31	0,001	0,008	0,022	0,969
22	-12,30	0,044	0,019	0,085	0,852
21	-13,25	0,418	0,354	0,106	0,121
20 $\pi$	-13,97	0,083	0,156	0,260	0,499
19	-14,17	0,231	0,006	0,159	0,604
18 $\pi$	-15,20	0,107	0,301	0,089	0,502

\*The contribution of the structural groups is equal to the sum of the squares of the coefficients in the atomic orbitals corresponding to a given structural fragment.

TABLE 3. Change in the Chemical Shifts ( $\Delta\delta$ , ppm) in the <sup>13</sup>C NMR Spectra of the Donor Molecule in Complexing with Maleic Anhydride

Donor	$C_{MA}$ , mole/ liter	$\delta, \Delta\delta$ ppm						
		C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	CH <sub>2</sub>	C <sub><math>\alpha</math></sub>	C <sub><math>\beta</math></sub>
	0	137,22	127,45	128,25	127,73	69,80	151,76	87,19
	1,54	-0,01	-0,22	-0,28	-0,16	-0,12	0	-0,21
	3,39	-0,05	-0,29	-0,33	-0,25	-0,15	+0,10	-0,31
	0	139,19	128,17	127,30	127,17	72,46	65,51	15,36
	0,93	+0,01	-0,04	-0,11	-0,08	+0,03	-0,08	+0,03
	2,27	+0,02	-0,12	-0,21	-0,17	+0,06	-0,13	+0,05
	0	116,40	100,30	100,80	98,14	-	1,67	-11,1
	1,95	-0,14	-0,08	-0,05	-0,03	-	+0,04	0
$C_{\beta}=C_{\alpha}-O-C^1-C^2-C^3-C^4$	0	40,10	4,30	-7,68	-13,46	-	124,82	58,18
	0,26	-0,08	0	0	0	-	0	-0,11
	0,49	-0,11	0	0	0	-	0	-0,14
	0,96	-0,12	0	0	0	-	0	-0,15
	0	129,49	89,49	102,00	97,49	-	120,68	67,21
	1,21	0	+0,04	-0,13	-0,12	-	+0,01	-0,15

Note. The minus sign indicates a shift toward the weak field; the plus sign, a shift toward the strong field.

<sup>13</sup>C NMR was used to test the hypothesis. Ethylbenzene, benzyl ethyl ether, BEVE, and PVE, which also form complexes with MA, were selected as analogs containing individual fragments of the ether molecule. A shift in the signals of the C atoms in the benzene ring of the VEBA molecule toward the weak field is observed in the presence of MA (Table 3). This change in the

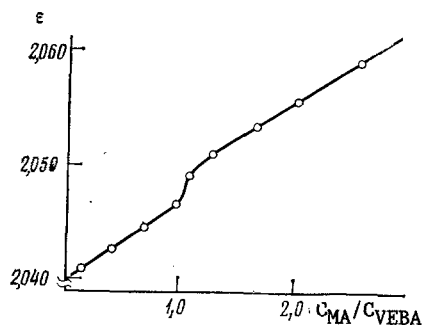


Fig. 1. Dependence of the dielectric constant on the ratio of the concentrations of monomers.

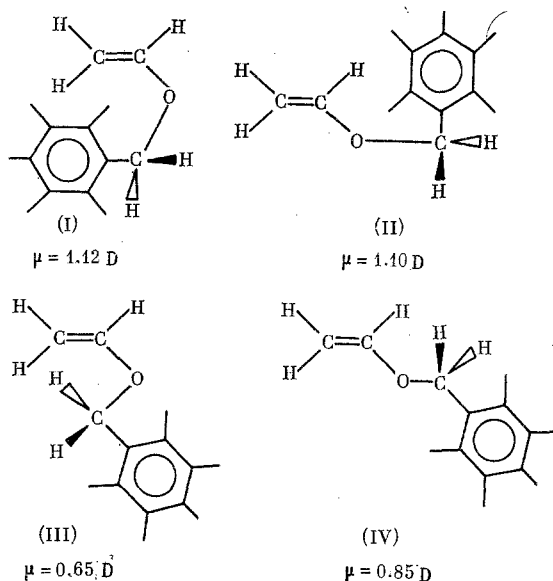
$^{13}\text{C}$  CS indicates a decrease in the electron density on the corresponding C atoms and the participation of the  $\pi$  system of the benzene ring in the DA reaction of the ether with the MA. The observed deshielding of the  $\text{C}_\beta$  atom of the vinyl group and the C atom of the  $\text{CH}_2$  group indicates the participation of the vinyloxy group in the DA reaction examined. The nature of the change in the CS of the benzene ring (see Table 3) is the same as in ethylbenzene, and the change in the shielding of the  $^{13}\text{C}$  nuclei of the vinyloxy group is similar to the effects for BVE. At the same time, good correspondence of the nature of the changes in the shielding of the  $^{13}\text{C}$  nuclei of the VEBA and PVE molecules in their coordination with MA is not observed. A stronger change in the CS is characteristic of the VEBA molecule, and the shift of the signal of the  $\text{C}^2$  atoms toward the weak field has a different direction.

The analysis of the NMR spectra indicates the participation of both the  $\pi$  system of the benzene ring and the  $\pi$  electrons in the double bond and the unshared pair of electrons in the O atoms of the vinyloxy group in VEBA in coordination with MA. However, as the results of the quantum-chemical calculations indicate, the observed change in the CS cannot be attributed to the presence of a common HOMO. It is possible to assume the formation of a VEBA:MA complex of the composition 1:2. To test this hypothesis, the composition of the complex formed was determined by dielectrometric titration in a solution of cyclohexane. The titration curve (Fig. 1) has a pronounced bend with a 1:1 concentration composition of the components, which indicates the formation of a complex of 1:1 composition, like the distinct linear dependence in the coordinates of the Ketelaar equation ( $r = 0.999$ ,  $s_0 = 0.0002$ ).

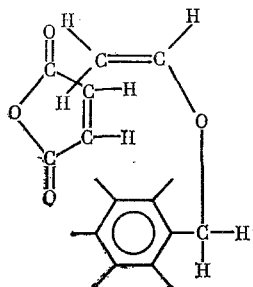
Such a change in the CS of the  $^{13}\text{C}$  nuclei of VEBA could also be caused by the formation of two types of complexes. Part of the ether molecule could participate in the DA reaction with MA due to the phenyl group and the other part could participate due to the vinyloxy group. This assumption is justified by the fact that the energies of the corresponding  $\pi$  orbitals are similar (cf. Table 2). If we begin with this model, then only a change in the CS of the C atoms in the benzene ring should be observed in the  $^{13}\text{C}$  NMR spectra in the case of the saturated analog of VEBA, benzyl ethyl ether (BEE). The unshared pair of the ether O atom should not make a significant contribution to the DA reaction with MA. In studying complexing of MA with dibutyl ether, a significant concentration of the DA complex was not found, and no changes take place in the shielding of the C atoms in the  $^{13}\text{C}$  NMR spectra.

In studying the electron spectra of solutions of BEE and MA in cyclohexane, the appearance of a new broad band in the 275 nm region was found, as in the case of VEBA, which indicates the formation of a DA complex. The study of the NMR spectra of the BEE-MA complex reveals the good coincidence of the changes in the chemical shifts of the  $^{13}\text{C}$  nuclei of the benzene ring.

The change in the shielding of the nuclei of the ethyl and methylene groups indirectly indicates the contribution of the unshared electron pair of the O atom to this reaction. As a consequence, the change in the CS of the  $^{13}\text{C}$  nuclei of VEBA and BEE in coordination with MA is due to the fact that the groups of the ether molecules have a position in space which allows the MA to simultaneously enter into the DA reaction with all fragments of the molecule. This conclusion is confirmed by the conformational analysis of the structure of VEBA. A comparison of the dipole moments of the possible conformers, theoretically calculated according to a vector-additive scheme, with the experimental value ( $\mu = 1.15$  D) showed that the best convergence of the  $\mu$  is observed for form (I).



The formation of DA complexes of VEBA with MA in a given steric position thus takes place due to charge transfer both from the HOMO of the phenyl group and from the HOMO of the vinyloxy group to the lowest unoccupied orbitals of the MA.



This charge transfer in the DA reaction of the monomers results in the formation of a complex whose structure causes the steric shielding of the C form in the double bond of the ether by the anhydride groups in MA in its reaction with the macroradical in the radical copolymerization reaction. The decrease in the reactivity of the vinyl group in the ether in the complex could also be due to the fact that it enters into the DA reaction with the double bond in the MA, bound by a DA bond to the benzene ring, which does not participate in polymerization; this should result in a decrease in the reactivity of the "complexed" monomers in the radical copolymerization reaction.

Based on the steric position of the acceptor and donor groups of the complex studied, it can thus be hypothesized that not all DA reactions can result in an increase in the reactivity of the monomers in the alternating copolymerization reaction.

#### CONCLUSIONS

1. The nature of the donor-acceptor complex of maleic anhydride with the vinyl ether of benzyl alcohol was studied by NMR, UV spectroscopic, dielectrometric titration, and quantum-chemical methods; the equilibrium constant was determined.
2. The formation of a  $\pi$  complex with weak charge transfer from the HOMO of the phenyl group and the HOMO of the vinyloxy group to the lowest unoccupied orbitals of the anhydride was demonstrated for the donor-acceptor reaction of maleic anhydride and the vinyl ether of benzyl alcohol.
3. In complexing of the vinyl ether of benzyl alcohol with maleic anhydride, the reactivity of the double bonds of the monomers is decreased in the copolymerization reaction, since the structure of the complex causes steric shielding of the C $\beta$  atom in the double bond in the ether by the anhydride groups.

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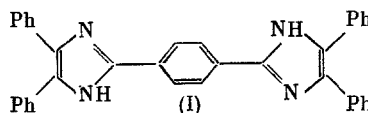
## RESEARCH IN THE FIELD OF 2,4,5-TRIARYLIMIDAZOLES.

COMMUNICATION 3. SPECTRAL-LUMINESCENCE PROPERTIES  
OF 1,4-BIS(4,5-DIPHENYL-1H-IMIDAZOL-2-YL)BENZENE

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In the work reported here, we continued our investigation [1, 2] of triarylimidazoles and their derivatives, which show promise for use in formulating photosensitive materials [3]. In order to establish the photophysical and photochemical mechanisms of reactions taking place in these systems under the influence of light, it is necessary to interpret the electronic absorption and emission spectra of the original molecules. Here we are reporting on a study of the spectral-luminescence properties of 1,4-bis(4,5-diphenyl-1H-imidazol-2-yl)benzene (I), which, according to [4], takes part in the process of photobleaching of solutions of 1,4-bis(4,5-diphenyl-2h-imidazol-2-ylidene)2,5-cyclohexadiene [4].



## EXPERIMENTAL

Compound (I), the 1,3-bis(4,5-diphenyl-1H-imidazol-2-yl)benzene, and the 2,4,5-triphenyl-1H-imidazole were synthesized in accordance with [5-7]. The spectral-luminescence measurements were performed on freshly prepared solutions of (I) at 293 and 77°K. As solvents we used purified benzene and purified 1-propanol glassed at 77°K, the latter also being used for the polarization measurements. The solution concentration was  $10^{-5}$  M.

The absorption spectra were recorded in a Specord UV-Vis spectrophotometer. The fluorescence spectra, the fluorescence excitation spectra, and the polarization dependences were obtained in a Jobin Yvon JY-3 spectrofluorimeter. The phosphorescence spectra, the phosphorescence excitation spectra, and also the polarization spectra and the dependence of the degree of polarization P on the phosphorescence wavelength were taken in a spectrometric unit that has been described in [8]. The degree of polarization was measured by a static technique. As the polarizer and analyzer we used Polaroid films. In determining P, we applied corrections for the polarizing effect of the monochromators, following [9]. The angles between the oscillator directions were determined in accordance with [10].

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