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Substituent-Induced Switch of the Role of Charge-Transfer Complexes in the Diels–Alder Reactions of *o*-Chloranil and Styrenes

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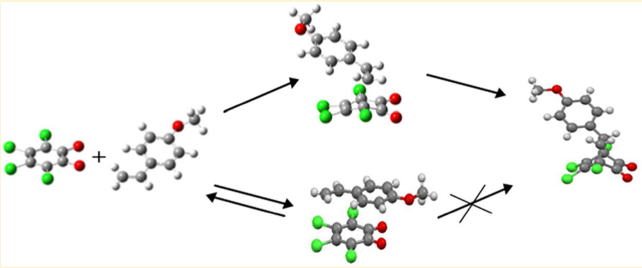
Supporting Information



ABSTRACT: Addition of *p*-substituted styrenes, XSty (X = H, Me, MeO, or Cl) to the solutions of *o*-chloranil, oCA, in dichloromethane resulted in the transient formation of the charge-transfer complexes, [XSty, oCA], followed by the Diels–Alder reaction. At low temperatures, these reactions led to formation of essentially pure endocycloadducts. As expected for the inverse-electron-demand Diels–Alder reaction, the rate constants of the cycloaddition rose with the increase of the donor strength. However, while facile cycloaddition took place in the neat mixtures of the *o*-chloranil with *p*-methyl, *p*-chloro-, or unsubstituted styrenes at low temperatures, a similar system involving the strongest MeOSty donor was surprisingly persistent. X-ray structural measurements and quantum-mechanical computations indicated that this anomaly is related to the fact that the diene/dienophile orientation in the charge-transfer [MeOSty, oCA] complex is opposite to that in the endocycloadduct and in the lowest-energy transition state leading to this isomer. Thus, the proceeding of the cycloaddition requires dissociation of the (dead-end) complex. For the systems involving the oCA diene and either the HSty, ClSty, or MeSty dienophile, the donor/acceptor arrangements in the charge-transfer complexes apparently are consistent with that in the corresponding products, and the formation of these complexes does not hinder the Diels–Alder reaction.

INTRODUCTION

The Diels–Alder reaction is one of the key processes in organic chemistry which has plentiful synthetic applications and played a central role in the development of organic reaction mechanisms.[1−4] Still, many aspects of this [4 + 2] cycloaddition, such as the role of pre-reactive association of the diene and the dienophile, remain a subject of continuing debate in chemical literature.[5−16] Indeed, mechanistic formulations of many bimolecular reactions include formation of metastable [1:1] encounter complexes as an important initial step.[16−18] The mixing of an electron-rich diene with an electron-deficient dienophile (or an electron-rich dienophile with an electron-poor diene in the inverse-electron-demand cycloaddition) frequently leads to the transient coloration of the solutions, indicating the formation of a charge-transfer (CT) complex between the donor (D) and acceptor (A). Moreover, in many series of diene/dienophile pairs, the rates of cycloaddition show apparent correlation with the thermodynamics of the CT complex formation and/or the energies of CT transitions.[19−25] These observations imply that CT complexes are essential intermediates in the subsequent cycloaddition (Scheme 1).[22−25] Alternatively, such [D,A] associates might be merely bystanders in the dead-end equilibrium in Scheme 2.[15]

$$\text{Scheme 1: } D + A \overset{K_{CT}}{\rightleftarrows} [D, A] \overset{k}{\rightarrow} \text{product} \tag{1}$$

$$\text{Scheme 2: } [D, A] \overset{K_{CT}}{\rightleftarrows} D + A \overset{k'}{\rightarrow} \text{product} \tag{2}$$

Earlier kinetic, structural, and computational studies led to the contradictory conclusions regarding this dichotomy.[3−16] The majority of these works relied primarily on the analysis of the kinetic features of the Diels–Alder cycloaddition. However, if a reaction mixture contains a large excess of one of the components (e.g., a donor), the steady-state consideration produces similar expressions for the experimentally measured rate constants:[15]

$$\text{For Scheme 1: } k_{exp} = K_{CT}k/(1 + K_{CT}[D]) \tag{3}$$

$$\text{For Scheme 2: } k_{exp} = k'/(1 + K_{CT}[D]) \tag{4}$$

Accordingly, these mechanisms are experimentally indistinguishable via steady-state kinetic measurements at constant temperature. To resolve this problem, Kiselev and Miller turned to the temperature dependence of the rate constants. They found that the apparent enthalpy of activation for the Diels–

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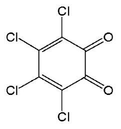
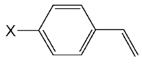
Alder reaction of tetracyanoethylene (TCNE) and 9,10-dimethylanthracene is negative and explained this observation by the involvement of a donor/acceptor complex according to Scheme 1.[7] Indeed, since the corresponding rate constant in eq 3 includes the K_{DA} term in the numerator, the negative enthalpy of the complex formation might overcompensate the positive activation enthalpies of the following cycloaddition. However, Houk et al. pointed out that cycloaddition reactions may exhibit a negative enthalpy of activation even in the absence of a donor/acceptor complex.[8] The careful non-steady-state analysis of the similar reaction by Parker and co-workers indicated that the kinetically significant intermediate which is formed with a relatively slow rate in the cycloaddition of TCNE and anthracene cannot be a charge-transfer complex.[13] Nevertheless, the structure of the intermediate suggested in their work is similar to a typical charge-transfer complex.[13,26−28]

While kinetic studies alone could hardly lead to a definitive mechanistic conclusion, elucidation of the role of charge-transfer complexes in the cycloaddition can be assisted by the X-ray structural characterization of the possible intermediates, including relevant prereactive associates.[15,26,29] Isolation and crystallographic studies of several such complexes, such as those formed by anthracene and the symmetric dienophile bis(*N*-ethylimino)-1,4-dithiin, revealed that mutual donor/acceptor arrangements within these associates are very well suited for their cycloaddition.[29] Thus, chemical transformation from the donor/acceptor pair to the corresponding transition state and to the cycloadduct requires minimal structural changes, which suggests that the diene/dienophile charge-transfer association facilitates the Diels−Alder reaction. In contrast, in the recent crystallographic study of the system involving anthracene and asymmetric 4-nitrobenzodifuroxan, Berrioni et al. found the opposite relationship.[15] For this pair, the charge-transfer complexes are characterized by the cofacial parallel arrangements of the diene and dienophile, while the cycloaddition products show perpendicular orientation of the corresponding moieties. Since the reactants in the complex are not suitably preoriented for a direct conversion into the expected cycloadduct, the solid-state CT associates are persistent. Accordingly, the authors concluded that these complexes have to dissociate back to reactants in order for the cycloaddition to occur; that is, CT associates are not intermediates in the Diels−Alder reaction.[15]

To determine if the latter conclusion is valid in a more general sense, and to clarify the role of the charge-transfer complexes in the Diels−Alder reaction, it is essential to establish the relation between the structures of the CT complexes and cycloaddition products in other reactions involving asymmetric reactants. In the search for such a system, we turned to the inverse-electron-demand Diels−Alder reactions between the *o*-chloranil acceptor, oCA, (3,4,5,6-tetrachlorocyclohexa-3,5-diene-1,2-dione) as a diene and the *p*-substituted styrene donors, XSty, as a dienophile.

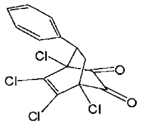


oCA

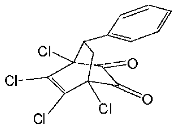


XSty (X = H, Cl, Me, OMe)

As was reported earlier, the thermal reaction of *o*-chloranil with styrene led to 1,4,5,6-tetrachloro-7-phenylbicyclo[2.2.2]-oct-5-ene-2,3-dione.[30,31] Although no structural data for this product are available, the asymmetric nature of the diene and the dienophile suggests that their [4 + 2] cycloaddition may lead to distinct endo- and exoadducts (structures I and II, respectively).Photochemical reaction of the same *o*-chloranil/styrene pair produced 5,6,7,8- tetrachloro-2,3-dihydro-2-phenyl-1,4-benzodioxin (structure III).[32]



I



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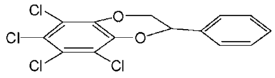


III

The charge-transfer complexes of *o*-chloranil with various donors, as well as the styrene associates with several organic acceptors, are also described in the literature.[24,25,33] For example, Ousaki et al. characterized complexes between various styrene donors and the tetracyanoethylene acceptor.[24,25] The authors suggested that these pre-reactive associates are intermediates in the cycloaddition reactions occurring in such systems. Similarly, the spectral and structural characterization of the charge-transfer complexes between *o*-chloranil and tetrathiafulvalene (TTF) revealed that the pre-reactive association plays a critical role in the oCA/TTF hetero-cycloaddition occurring via the donor/acceptor electron-transfer step.[33,34]

Thus, the earlier observations of the cycloaddition and donor/acceptor associations involving *o*-chloranil and/or styrene molecules indicate that this diene/dienophile pair represents a suitable system for the evaluation of the role of charge-transfer complexes in the Diels−Alder reaction. Importantly, the donor/acceptor interactions and the kinetics of cycloaddition in these systems can be modulated via variation of the substituents in the XSty molecule. Most of all, the asymmetry of the reactants implies the possibility of diverse stereochemistries of complexes and cycloadducts and provides an opportunity to evaluate the structural relationship between species along the reaction coordinate. In fact, the results of the spectral, structural, and computational studies presented in the current work indicate that the variation of the substituent in the *para*-position of the styrene molecule drastically affects this relationship and, accordingly, the function of the charge-transfer complexes in the [4 + 2] cycloaddition in the oCA/XSty systems.

■ RESULTS AND DISCUSSION

Spectral and Structural Characterization of the Styrene/*o*-Chloranil Complexes. *Spectral Identification of the Donor/Acceptor Complexes.* The *o*-chloranil acceptor is characterized by an absorption band at λ_{max} = 457 nm, which is responsible for the yellow-red color of its solutions in dichloromethane. When excess amounts of the colorless MeOSty donor were added to such solutions, they turned darker (at low temperatures and at high concentrations of MeOSty, the solutions were nearly black). This change in coloration was related to the appearance of a new absorption band with a maximum at 597 nm (Figure 1).[35] At room temperature, intensities of the bands at 457 and 597 nm gradually decreased (depending on concentration of the MeOSty, their half-lives were from 2 to 30 min, vide infra). At low temperature (e.g., at −40 °C), the coloration of the MeOSty/oCA solutions in dichloromethane was persistent during the time of measurements. Furthermore, the decrease of

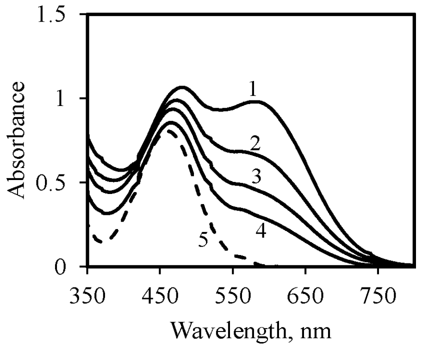


Figure 1. Temperature-dependent absorption of the dichloromethane solution of the oCA acceptor (5 mM) and the MeOSty donor (0.36 M) showing the band of the [MeOSty, oCA] complex at 597 nm. Temperatures (in °C): −95 (1), −77 (2), −58 (3), and −39 (4). The dashed line (5) represents a spectrum of the solution containing only the oCA acceptor.

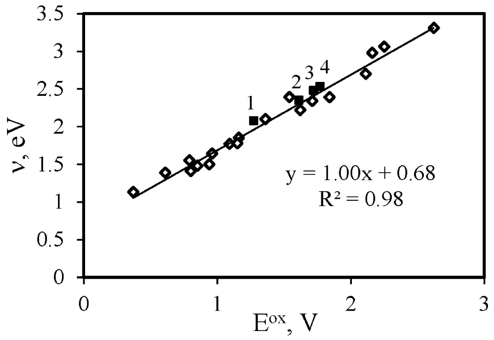


Figure 2. Mulliken correlation of the energy of charge-transfer transition of the complexes of *o*-chloranil with organic donors. Black squares represent complexes with styrenes (1, MeOSty; 2, MeSty; 3, ClSty; 4, Sty), and open rhombuses correspond to complexes with the other organic donors (from ref 33; see Table S1 in the Supporting Information for details).

the temperature from −40 to −95 °C resulted in the significant increase of intensity of the band with a maximum at 597 nm (Figure 1). Importantly, the variation of the absorption intensity in the 550−650 nm range with temperature was reversible.

The measurements of the absorption intensity at 597 nm at various concentrations of the donor and acceptor using Job's method[36] established the formation of the 1:1 complex according to eq 5.

$$\text{MeOSty} + \text{oCA} \rightleftarrows [\text{MeOSty, oCA}] \qquad (5)$$

The quantitative treatment of the absorption data measured at various concentrations of MeOSty and oCA in the temperature range from −35 to −95 °C (see Figure S1 in the Supporting Information) led to the thermodynamic parameters: ΔH_{CT} = −2.1 kcal mol^{-1} and ΔS_{CT} = −12.5 cal mol^{-1} K^{-1} for the equilibrium in eq 5, and to the extinction coefficient of the [MeOSty, oCA] complex $\varepsilon_{CT} = 1.0 \times 10^4$ M^{-1} cm^{-1}.

The additions of the other styrene donors to the dichloromethane solutions of *o*-chloranil led to a similar increase of intensity of absorption in the 500−600 nm range. In general, the behaviors of the resulting solutions were similar to those containing MeOSty/oCA mixtures. At low temperatures, their colorations were persistent, and the intensity of the new absorption bands increased reversibly with lowering temperature. At room temperature, the absorption of [XSty, oCA] complexes and that of the oCA acceptor gradually disappeared, although the discolorations were slower than that of the solution with MeOSty (vide infra). With these donors, however, the new absorption bands overlapped with the absorption of the *o*-chloranil itself, and their positions were obtained via spectral subtraction.[37] This procedure led to the absorption bands maxima at 490, 500, and 528 nm for complexes of *o*-chloranil with HSty, ClSty, and MeSty, respectively. Figure 2 demonstrates that the energies of the absorption band of the [XSty, oCA] complexes show clear correlation with the oxidation potentials of the XSty acceptors, which were obtained from the CV measurements (see Table S1 in the Supporting Information for details). Moreover, these absorption bands follow the same Mulliken dependence as those measured for complexes of *o*-chloranil with other common organic donors, which indicates the charge-transfer nature of the [XSty, oCA] complexes.[27,33]

X-ray Crystallography of the [MeOSty, oCA] Complex. Slow diffusion of hexane into dichloromethane solutions containing *o*-chloranil and *p*-methoxystyrene at −65 °C resulted in formation of black crystals suitable for crystallographic studies (see the Experimental Section for details). X-ray measurements revealed that they are characterized by an orthorhombic unit cell in space group *Pna*2(1) which contains molecules of the oCA acceptor and the MeOSty donor in 1:1 stoichiometry. These molecules form alternating stacks (Figure 3A) consisting of nearly coplanar donor/acceptor pairs with the interplanar separation of ~3.20 Å.[38] The vinyl groups of the styrene molecules in such complexes are arranged over the chlorine sides of the acceptors, and their methoxy substituents are directed over the oxygen sides of the oCA counterparts. Close donor/acceptor arrangements lead to multiple interatomic C−C contacts of 3.15−3.25 Å that are significantly shorter than the sum of their van der Waals radii of 3.40 Å. In comparison, the interplanar separation between the *o*-chloranil molecule and the other neighboring MeOSty moiety is about 3.35 Å, and their closest C−C contact is 3.320(5) Å.

The short interplanar separations and interatomic contacts in the MeOSty/oCA pairs are similar to that in common charge-transfer complexes,[26] and they indicate strong intermolecular donor/acceptor interaction. To check if such interaction results in a noticeable donor/acceptor charge transfer, we followed our previous study[33] and compared geometric characteristics of the oCA moieties in the [MeOSty, oCA] complex with the relevant values established earlier for the separate neutral molecules and corresponding ion radicals (Table 1).[39]

The bond length values in Table 1 indicate that the *o*-chloranil's geometry in the [MeOSty, oCA] associate is close to that of the neutral acceptor. However, a closer scrutiny of the data revealed that the single and double bond lengths in the *o*-chloranil ring deviate somewhat from the related values in the neutral molecule toward that in the corresponding anion radical. In particular, the single C−C bonds (β, γ, and ε in Table 1) are shortened, and its double C═C bonds (δ) are elongated in the oCA moiety in the [MeOSty, oCA] complex as compared to their values in the separate oCA molecule. The directions of these changes are consistent with those occurring upon reduction of the oCA acceptor. The application of the Pauli's bond length/bond order relationship (in the same way as described earlier for the complex of *o*-chloranil with the tetrathiafulvalene donor[33]) points to charge transfer of ~0.1*e* in

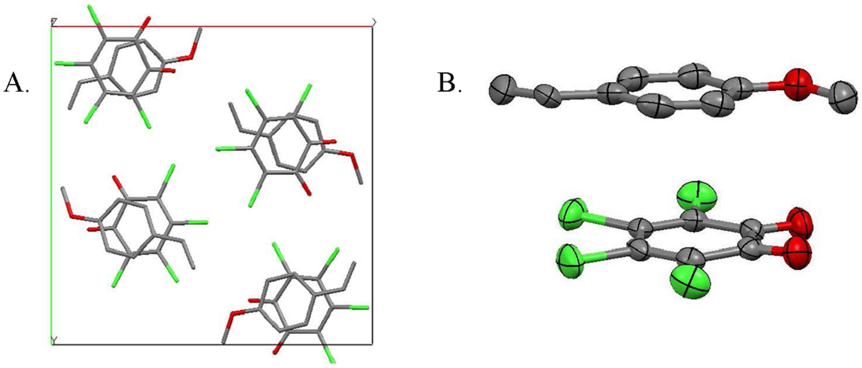
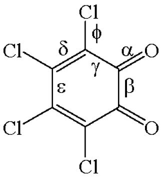


Figure 3. (A) Crystal structure of the [MeOSty, oCA] complex viewed along the *c* axis. (B) Side perspective view of the [MeOSty, oCA] complex (ellipsoids are drawn at 50% probability, hydrogen atoms are not shown for clarity).

Table 1. Average Bond Lengths^a within oCA Moieties in the [MeOSty, oCA] Complex in Comparison with Those in Related Neutral Molecules and Ion Radicals



structure	α	β	γ	δ	ε	ϕ^a
oCA/MeOSty^a	1.206(4)	1.533(4)	1.469(4)	1.359(5)	1.471(5)	1.701(4)
oCA^b	1.209(6)	1.549(6)	1.474(8)	1.350(6)	1.476(6)	1.705(6)
oCA$^{-\bullet c}$	1.234	1.517	1.453	1.381	1.425	1.758

[a] In parentheses, standard deviations calculated based on both the esd of individual bond lengths and variations of crystallographically non-equivalent bonds. [b] Averaged over 8 crystallographically independent molecules.[33] [c] From DFT calculations.[33]

the [MeOSty, oCA] complex (see Table S2 in the Supporting Information for details).[39,40]

In contrast to the system with *p*-methoxystyrene, low-temperature crystallizations from the solutions containing *o*-chloranil and either Sty, ClSty, or MeSty styrene resulted in the formation of the crystals of the corresponding cycloaddition products and/or the separate oCA acceptor.

Kinetics of the Diels–Alder Reaction and Structural Characterization of the Products. *Kinetic Characteristics of the oCA/XSty cycloaddition.* When excess of any of the XSty donors was added to the dichloromethane solution of the oCA acceptor at room temperature, the absorption of the [XSty, oCA] complex, as well as the absorption band of *o*-chloranil gradually disappeared and a new less intense absorption band at ~440 nm was formed (see Figure S2 in the Supporting Information). Accordingly, the coloration of the solution changed from dark-red to bright-yellow. The quantitative comparison of the low-intensity band with the spectral characteristics of the isolated crystalline product of oCA/XSty cycloaddition (vide infra) confirmed practically 100% completion of the Diels–Alder reaction.

In the mixtures with a large excess of the styrene donors, the changes of the absorption intensity in the visible range with time were well-described by the pseudo-first-order equation with the single rate constant, k_{obs}, from the start to the completion of reaction:

$$A(t) = A_0\exp(-k_{obs}t) + A_\infty[1 - \exp(-k_{obs}t] \qquad (6)$$

where A_0 is a starting absorption and A_∞ is a final absorption values at a certain wavelength (see Figure S3 in the Supporting Information). At different wavelengths, the values of A_0 were related mostly to the absorption of *o*-chloranil (e.g., if absorption is measured at 440 nm) or by its complex with donors (e.g., if measurements were carried out at 550 nm), or their combination.[41] The values of A_∞ corresponded to the absorption of the product of cycloaddition (i.e., $A_\infty = c_0\varepsilon_{CA}l$, where c_0 is a starting concentration of oCA and ε_{CA} is an extinction coefficient of the cycloadduct obtained from the measurements of the solution of the corresponding crystalline materials, vide infra). It indicates that the rate of reverse reactions, that is, dissociation of the cycloadducts, is negligible under the conditions used in the kinetic measurements.

For the reactions of *o*-chloranil with various styrenes, the values of k_{obs} increased linearly with the concentration of a donor (see Figure S4 in the Supporting Information). The slopes of these dependences resulted in the second-order rate constants, k_{exp} (in 10^{-4} M^{-1} s^{-1}): 50, 13, 3, and 2 for the reactions of *o*-chloranil with MeOSty, MeSty, HSty, and ClSty, respectively.[41] As expected for the cycloaddition involving electron acceptors as a diene and electron donors as a dienophile (i.e., inverse-electron-demand Diels–Alder reaction), the highest rate constant was found in the reaction of *o*-chloranil with the most electron-rich *p*-methoxystyrene. Furthermore, the activation energy for the oCA/MeOSty reaction of E_a = 8.4 kcal mol^{-1} (evaluated from the temperature dependence of the rate constant in the 10–30 °C range; see Figure S4 in the Supporting Information) was somewhat lower than the value E_a = 11.0 kcal mol^{-1} measured for the oCA/HSty cycloaddition.

Preparation and Structural Characterization of Cycloaddition Products. Preparative Diels–Alder reactions were carried out under air- and moisture-free conditions (to avoid

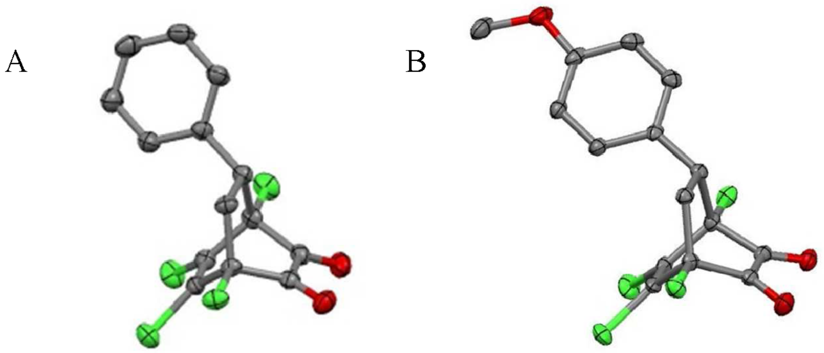


Figure 4. X-ray structures of the Diels−Alder cycloaddition products of *o*-chloranil with styrene (A) and *p*-methoxystyrene (B) (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50%).

formation of hydrated byproduct)[42] either in dichloromethane at −35 °C or by mixing neat reactants at 0 °C. In most cases, these two procedures afforded the same cycloaddition products, as established by X-ray crystallography and NMR spectroscopy in high yields of 93−97%.

In particular, mixing 500 mg (∼0.02 mol) of *o*-chloranil with equimolar amount of styrenes, XSty, where X = 4-MeO, Me, H, or Cl, in ∼5 mL of dichloromethane at low temperature resulted in immediate formation of dark-red solutions. After these solutions were kept in a refrigerator at −30 °C for several days, they turned yellow, and bright-yellow powders were precipitated by addition of hexane. Slow diffusion of hexane into these dichloromethane solutions afforded single crystals suitable for X-ray measurements (see the Experimental Section for details).

X-ray crystallographic analysis showed that the yellow crystals represented the products of XSty/oCA cycloaddition (Figure 4 and Figure S5 in the Supporting Information). Noticeably, all of these adducts were endoisomers in which aromatic rings of the styrene fragments were located over the double bonds formed on the chlorine-substituted side of the *o*-chloranil fragments. Furthermore, NMR measurements confirmed uniform composition of the products and their essential purity on the NMR scale (see Figure S7 in the Supporting Information).

Alternatively, cycloaddition was carried out by a careful mixing of equimolar amounts of neat styrenes and *o*-chloranil at low temperatures. For example, mixing 270 μL (2.05 mmol) of MeSty and 500 mg (2.03 mmol) of oCA under nitrogen atmosphere at ∼0 °C resulted in formation of the dark-red mixture, which was kept in a refrigerator at 0 to 5 °C. After 20 h, a bright-yellow crystalline product was formed, and unit cell measurements confirmed that the structure of the product was the same as obtained in the corresponding dichloromethane solutions. UV−vis and ^{1}H NMR measurements of this material further confirmed that the MeSty/oCA adduct obtained via reaction of neat compounds was the same as that obtained via reaction in dichloromethane. In a similar way, neat mixtures of *o*-chloranil with either Sty or ClSty afforded the cycloaddition products, although completion of the reactions with these weaker donors required, as expected, longer time than that with MeSty. However, it was quite surprising to find that the mixture of *o*-chloranil with *p*-methoxystyrene, for example, 270 μL (or 2.03 mmol) of MeOSty and 500 mg of oCA, prepared and stored at ∼0 °C in exactly the same way as that with *p*-methylstyrene, remained dark-red for several days. When this mixture was dissolved at low temperature in dichloromethane, its UV−vis spectral analysis showed the presence of >90% of the original *o*-chloranil, and warming up resulted in the formation of the cycloaddition products. To verify this unexpected stability of the neat oCA/MeOSty mixtures, the equimolar amounts of the *o*-chloranil with either *p*-methylstyrene or *p*-methoxystyrene were mixed at −78 °C in dichloromethane, and the solvent was eliminated from both systems by low-temperature in vacuo evaporation. Afterward, the resulting mixtures were kept at −35 °C. In 2 days, the mixture with *p*-methylstyrene turned yellow and its dissolution showed nearly quantitative formation of the cycloaddition product. In contrast, the oCA/MeOSty mixture remained dark-red after the same period of time.

Finally, the black crystals of the [MeOSty, oCA] complex which were prepared for X-ray structural measurements by slow diffusion of hexane into dichloromethane solutions containing *o*-chloranil and large excess of the MeOSty donor (vide supra) were stable when kept at low temperature for several weeks. Moreover, the analogous black powder (obtained by the fast addition of hexane to the similar oCA/MeOSty solutions in dichloromethane at −78 °C) was also persistent when stored at low temperature. Dissolving this powder in dichloromethane at −60 °C showed more than 90% recovery of the original *o*-chloranil (which indicated that no significant amount of the cycloadduct was formed). When this solution was warmed up, it turned yellow, and its spectrum showed formation of the cycloaddition product. This confirms that, similar to the [MeOSty, oCA] complex, the black powder contains both oCA and MeOSty components. The persistency of these oCA/MeOSty systems contrasts the facile chemical transformations occurring (under similar conditions) in the neat mixtures of *o*-chloranil with MeSty, ClSty, and Sty donors. In the search for the reason of such drastic distinctions, we turned to the computational evaluation of energetics of reactants, products, and intermediates pertinent to this transformation.

Computational Analysis of the Diels−Alder Reaction of *o*-Chloranil with Styrene Donors. Structures of the reactants, products, and transition states for the Diels−Alder reaction between *o*-chloranil and various styrenes were optimized at B3LYP/6-311+G(d,p) level using the Gaussian 03 program (see the Experimental Section for details).[43] The energies of the endo- and exoadducts of the Diels−Alder reaction (calculated with respect to the sum of the energies of the most stable conformations of corresponding reactants) are listed in Table 2, and structural details of the reactants and products of cycloaddition are presented in the Supporting Information.

Table 2. Energies of the Products of Cycloaddition for Various oCA/XSty Pairs[a]

X	H	Me	Cl	MeO
endoadduct	−9.6	−9.7	−9.5	−9.6
exoadduct	−8.9	−8.6	−8.6	−8.7
heteroadduct	−20.36/−22.9[b]			

[a] In kcal/mol, with respect to the sum of the energies of the most stable conformations of corresponding reactants; from B3LYP/6-311+G(dp) computations, including unscaled zero-point energy (ZPE) corrections and solvation energies in dichloromethane. [b] See the Supporting Information for the corresponding structures of heteroadducts.

The data in Table 2 indicate that the endoisomers resulting from the normal Diels−Alder reaction are more stable than the corresponding exoisomers for all oCA/XSty pairs, but the energy difference is only about 0.7−1.1 kcal mol^{-1}. These differences are too small to account for the formation of essentially pure (on the NMR scale) endoadducts. Furthermore, for the oCA/HSty pair, the energies of the products of heterocycloadditions are about 11 kcal/mol lower than that of their normal Diels−Alder reaction.[44] Still, no heteroadducts were detected in the thermal reaction. These computational results indicate that the preferable formation of the endoadduct is not related to the thermodynamic factors.

The TS structures leading to the endo- and exoisomers of the normal Diels−Alder reaction between *o*-chloranil and styrene are illustrated in Figure 5. These TS are asynchronous: the endo-TS in Figure 5A is characterized by the distances of 2.755 and 1.960 Å between carbons forming new σ-bonds, and the corresponding values in the exo-TS are slightly higher (2.792 and 1.967 Å). Calculations of the atomic charges via natural population analysis (NPA) phase of natural bond orbital analysis indicate that both TS structures involve significant charge transfer from HSty donor to oCA acceptor of ~0.35 (see Table S4). Noticeably, at B3LYP/6-311+G(dp) level, the energy of the transition state leading to the endoadduct is about 1.3 kcal lower than that of the exo-TS (see Table S3 in the Supporting Information). Since B3LYP computations frequently underestimate long-rate attraction (dispersion),[45] the energies of the transition states leading to endo- and exoadducts were recalculated using the MP2 method. The single-point MP2/6-311+G(dp) calculations using B3LYP/6-311+G(dp)-optimized TS structures resulted in the energy of the endo-TS which is about 2.2 kcal/mol lower than that of the exo-TS analogue. For the MeOSty/oCA and ClSty/oCA pairs, B3LYP/6-311+G(dp) computations produced TS structures for the Diels−Alder reaction which are similar to that with styrene donor (see the Supporting Information). Due to the presence of electron-donating or -withdrawing substituents, the charge transfer (calculated via NBO analysis) was somewhat higher in the transition states involving MeOSty donor (0.43) than that in the TS with styrene, and the corresponding values for the ClSty are slightly lower (0.34). Most importantly, the B3LYP/6-311+G(dp) computations for the MeOSty/oCA and ClSty/oCA pairs resulted in the energies of the TS leading to the endoadducts that are about 1.3 kcal/mol lower than that leading to the exoisomer, while the differences at MP2/6-311+G(dp) are about 2.3 kcal/mol (see Table S4 in the Supporting Information for details).

If all other factors are similar (as could be expected in the formation of the endo- and exoisomers), the difference in the transition-state energies of 2.2−2.4 kcal/mol suggests that the rate constant for endoproduct formation at low temperatures (e.g., at 0 °C or at −35 °C) is about 100 times higher than that leading to the exoisomers.[46,47] Furthermore, the energy of the TS leading to the hetero-DA reaction (obtained via single-point MP2/6-311+G(dp) calculation of the TS structure optimized at B3LYP/6-311+G(dp) level) is more than 12 kcal/mol higher than that leading to the endoadduct of the normal DA (see the Supporting Information for the details of the hetero-TS structure). On the whole, the differences in TS energies are sufficient to account for the formation of the essentially pure endoisomer at low temperatures employed in our synthesis.

Structural (Dis)similarity of the Charge-Transfer Complexes and TS as a Key Factor Determining the Diels−Alder Reaction Pathway. The [4 + 2] oCA/XSty cycloaddition represents an example of the inverse-electron-demand Diels−Alder reaction. The rate constants for such processes are expected to rise as a donor ability of the dienophile increases. The reactions between the oCA acceptor and *p*-substituted styrenes in dichloromethane follow, in general, this trend. However, while the neat mixtures of oCA with ClSty, HSty, and MeSty also showed a similar tendency (i.e., the fastest formation of the yellow cycloaddition products at 0−5 °C was observed with the relatively electron-rich *p*-methylstyrene), the strongest MeOSty donor does not react with *o*-chloranil under similar conditions. Spectral, structural, and computational data obtained in the current work allow clarification of the anomalous behavior of the MeOSty/oCA pair and, more generally, elucidate the variable role of the charge-transfer complexes in the Diels−Alder reactions.

The X-ray structure of the [MeOSty, oCA] charge-transfer complex shows the methoxy group of the styrene located over oxygen-substituted side of *o*-chloranil (Figure 3B). In contrast, in the most stable TS leading to the prevailing endoadduct, the methoxy substituent is directed over the chlorine side of the *o*-

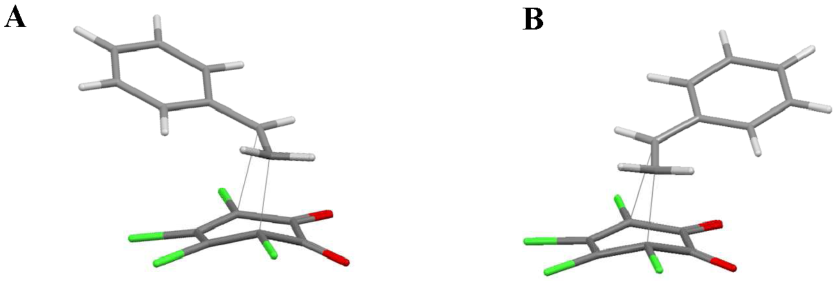
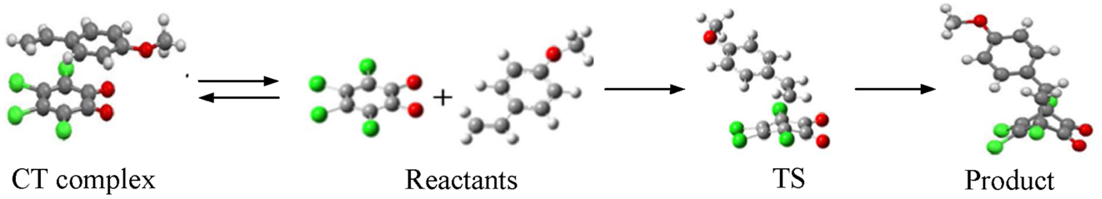
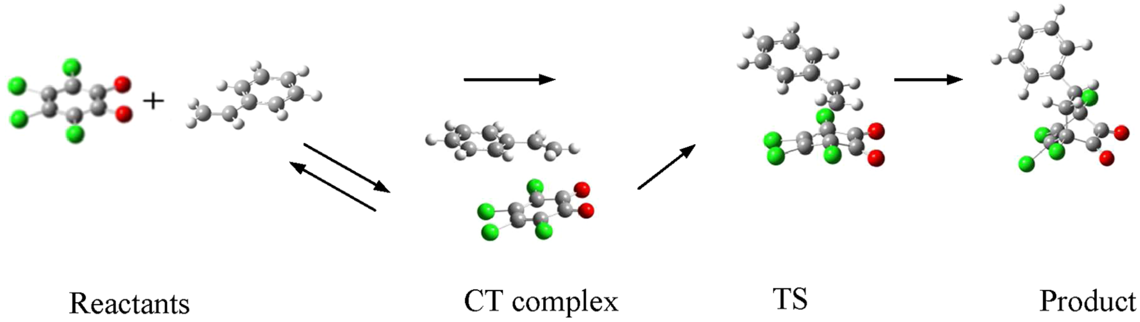


Figure 5. Transition states leading to endo- and exoisomers of DA reaction between *o*-chloranil and styrene (from B3LYP/6-311+G(dp) calculations; see the Experimental Section for details).

Scheme 3



Scheme 4



benzoquinone (Figures 4B and 5A). Thus, the relative orientation of the oCA and MeOSty moieties in a donor/acceptor associate is not suitable for the Diels−Alder reaction. As such, dissociation of the complex and the rearrangement of the MeOSty and oCA reactants are required in order for their cycloaddition to take place (Scheme 3).

In the dichloromethane solutions at room temperature, the concentrations of the transient [XSty, oCA] complexes are relatively small, so their presence does not affect significantly the kinetic features of the cycloaddition.[48] In the neat mixtures of *o*-chloranil with styrenes, however, the formation of such complexes is critical. When neat reactants are mixed at low temperatures, the spontaneous formation of charge-transfer complexes is much faster than the cycloaddition. The dissociation of the [MeOSty, oCA] complex is apparently not favorable under such conditions, so these CT complexes are stable, and cycloadduct formation is suppressed.

In comparison, the facile cycloadditions were observed in the mixtures of neat MeSty, ClSty, and HSty with oCA at low temperatures, and our efforts to grow single crystals of complexes of *o*-chloranil with the MeSty, ClSty, and HSty donors were unsuccessful (vide supra). Quantum-mechanical computations suggest that the relative donor/acceptor orientation within these associates is opposite to that in the [MeOSty, oCA] complex. For example, the most stable structure of the [HSty, oCA] complex shows the vinyl group directed toward oxygen side of the *o*-chloranil acceptor (see Table S4 and Figure S9 in the Supporting Information). Notably, such donor/acceptor orientation is similar to that in the most stable transition state leading to the endocycloadduct (Figure 5A). As a result, minimal structural changes are involved in transformation of the [HSty, oCA] dyad into the TS leading to the endocycloadduct, and the TS may be reached either via direct reactant encounter or via their charge-transfer complex (Scheme 4; see the corresponding energies in the Scheme S1 in the Supporting Information).[49]

On the whole, our data indicate that reactivity of the neat XSty/oCA mixtures is determined by the relationship of the donor/acceptor orientations in the charge-transfer complexes and the lowest-energy TS structures for their Diels−Alder reactions. It should be noted in this respect that the HOMO/LUMO interactions in the transition states for the DA reaction involve the bonding/mixing of the diene's and the dienophile's orbitals, which is akin to that in the charge-transfer complexes.[3,4,27] Due to similar frontier orbital interactions, the structures of the CT complexes and TS for the Diels−Alder reaction are expected to be comparable for the majority of the diene/dienophile pairs,[50] and this similarity facilitates conversion of the donor/acceptor associates into the cycloaddition products. As such, only a few CT complexes between the diene and the dienophile are stable enough to allow their isolation and X-ray crystallographic characterization. However, the HOMO/LUMO shapes for the XSty and oCA molecules suggest that the bonding overlap of the frontier orbitals may occur at different donor/acceptor arrangements (Figure S8 in the Supporting Information), and quantum-mechanical computations produced two local minima for XSty/oCA associates (Figure S9). Electrostatic interactions, repulsion of the filled orbital, dispersion, and other factors which determine energies of these loose associates depend on the *p*-substituent in the styrene donors, so the lowest-energy donor/acceptor arrangement may differ for various XSty/oCA dyads. In particular, the analysis of the surface electrostatic potentials suggests that the experimental "exo" structure of the [MeOSty, oCA] complex is stabilized by the attraction between the areas of negative potential around the oxygens in the oCA molecule and the area of positive potential around the methyl group of the methoxy substituent (Figure S10 in the Supporting Information). With the other *p*-substituents, such stabilization is lacking, and the "endo" donor/acceptor orientation is favored (Figures S9 and S10).[49] On the other hand, the lowest-energy transition states for the Diels−Alder reactions are similar for all XSty/oCA pairs, as verified by the consistent formation of the endoisomer. Thus, switching from the unsubstituted (or methyl- or chlorine-substituted) styrene to the MeOSty donor changes the relationship between the structures of CT complexes and transition states and, accordingly, the function of such complexes in the Diels−Alder reaction.

CONCLUSIONS

The structural studies of the products of the inverse-electron-demand Diels–Alder reaction involving *o*-chloranil and various styrenes showed consistent formation of the endocycloadduct in which the *p*-substituents of styrene directed toward the chlorine-substituted side of the *o*-chloranil fragment. Quantum-mechanical computations indicated that this stereoselectivity is related to the lower energy of the TS leading to the endoisomers relative to the TS, resulting in the corresponding exoadducts. In comparison, the X-ray crystallographic study revealed that the charge-transfer [MeOSty, oCA] complex, which is formed spontaneously upon addition of *p*-methoxystyrene to *o*-chloranil, is characterized by the opposite orientation of the reactants, that is, the methoxy group directed toward the oxygen-substituted side of *o*-chloranil. Accordingly, for the MeOSty/oCA pair, the cycloaddition reaction may proceed only directly from reactants, and the charge-transfer complex represents a by-stander in this process. Moreover, if the [MeOSty, oCA] complex predominates and its dissociation is unfavorable (e.g., in the mixture of neat reactant at low temperatures), the cycloaddition is inhibited. For the systems involving the oCA acceptor and either a HSty, ClSty, or MeSty donor, the diene/dienophile arrangements in the CT complexes are apparently consistent with that in the corresponding transition state, and the formation of these complexes does not hinder the Diels–Alder reaction. As a whole, the study of the series of asymmetric diene and dienophile, XSty/oCA, pairs demonstrated that the role of the charge-transfer complexes in the Diels–Alder reaction is determined by the structural relationshiop between the complexes and the corresponding transition states. Consequently, relatively minor changes in reactants which induce the variation of the structure of the CT complex (such as the replacement of the *p*-substituent in the styrene donor) result in the switch of the function of this associate in the [4 + 2] cycloaddition.

EXPERIMENTAL SECTION

Materials. Commercially available *o*-chloranil was purified by sublimation. Styrene, *p*-chlorostyrene, *p*-methoxystyrene, and *p*-methylstyrene were distilled at low pressure. Dichloromethane (HPLC grade) was freshly distilled over CaH_2, and hexane was distilled over sodium/benzophenone under a dry nitrogen atmosphere and briefly stored over a potassium or sodium mirror. Cycloaddition reactions of various styrene donors with the *o*-chloranil acceptor were carried out in well-dried Schlenk tubes (25 mL) under dry nitrogen atmosphere. Any admixture of water resulted in formation of the monohydrated product.[42]

1,4,5,6-Tetrachloro-7-phenylbicyclo[2.2.2]oct-5-ene-2,3-dione (1). Five hundred milligrams of *o*-chloranil (2.03 mmol) was dissolved in 5 mL of dichloromethane in a 25 mL Schlenk tube under dry nitrogen atmosphere. This solution was cooled to −35 °C, and 240 μL of styrene (2.09 mmol) was added. The resulting dark-red solution was placed in a refrigerator (−30 °C). After 1 week, the solution turned yellow, and the addition of hexane resulted in precipitation of yellow powder, which was filtered, washed with pentane, and dried in vacuum (yield 670 mg, 96%): mp 133−135 °C (lit. 133 [30]); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39 (m, 3H), 7.14 (m, 2H), 3.57 (dd, J = 10.3, 5.8 Hz, 1H), 3.07 (dd, J = 14.3, 10.3 Hz, 1H), 2.88 (dd, J = 14.3, 5.7 Hz, 1H); FT-IR ν_{max} 1763, 928, 765, 704 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} = 444 nm, ε = 2.1 × 10^2 M^{-1} cm^{-1}. Slow diffusion of hexane into the reaction solution afforded bright-yellow crystals suitable for the X-ray crystallographic analysis. X-ray structure of this HSty/oCA adduct is shown in Figure 4A (see crystallographic data in the Supporting Information). Alternatively, 240 μL of neat styrene was carefully mixed with 500 mg of oCA in a 25 mL Schlenk tube at 0 °C under a dry nitrogen atmosphere, and the resulting dark-red liquid was placed in a refrigerator (0−5 °C). After 1 day, this mixture turned into a yellow crystalline material. The product was washed with pentane and dried in vacuo (yield 680 mg, 97%). Spectral (UV−vis, FT-IR, and ^{1}H NMR) characteristics of this product were the same as those of the product of cycloaddition formed in dichloromethane solution, and unit cell measurements confirm that the structures of both products are identical.

1,4,5,6-Tetrachloro-7-(4-chlorophenyl)bicyclo[2.2.2]oct-5-ene-2,3-dione (2). As with styrene, the cycloaddition reaction was carried out by addition of 250 μL of *p*-chlorostyrene (2.08 mmol) to the solution of 500 mg of oCA in dichloromethane at −30 °C, or by mixing neat reactants at 0 °C. Both methods produced a yellow crystalline material (740 mg, 96% from solution and 755 mg, 98% from the reaction with neat reagents): mp 139−141 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 3.57 (dd, J = 10.5, 5.8 Hz, 1H), 3.07 (dd, J = 13.8, 10.2 Hz, 1H), 2.81 (dd, J = 14.4, 5.7 Hz, 1H); FT-IR ν_{max} 1759, 1568, 1096, 824, 754 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} = 444 nm, ε = 2.1 × 10^2 M^{-1} cm^{-1}. Anal. Calcd for $C_{14}H_9Cl_5O_2$: C, 43.74; H, 1.84. Found: C, 43.62; H, 1.86. X-ray structure of this ClSty/oCA adduct is presented in Figure S5 in the Supporting Information.

1,4,5,6-Tetrachloro-7-(4-methylphenyl)bicyclo[2.2.2]oct-5-ene-2,3-dione (3). This MeSty/oCA adduct was obtained via reaction of 270 μL (2.05 mmol) of *p*-methylstyrene with 500 mg of *o*-chloranil in dichloromethane at −30 °C, or in a mixture of neat reagents (yield 705 mg, 96%): mp 160−163 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.2 (d, J = 9.6 Hz, 2H), 7.1 (d, J = 8.4 Hz, 2H), 3.55 (dd, J = 10.3, 6.3 Hz, 1H), 3.06 (dd, J = 14.1, 10.8 Hz, 1H), 2.84 (dd, J = 14.1, 6.6 Hz, 1H), 2.33 (s, 3H); FT-IR ν_{max} 2916, 1761, 1570, 822, 752 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} = 444 nm, ε = 2.0 × 10^2 M^{-1} cm^{-1}. Anal. Calcd for $C_{15}H_{12}Cl_4O_2$: C, 49.49; H, 2.77. Found: C, 48.81; H, 2.84. X-ray structure of the product is presented in Figure S5 in the Supporting Information.

1,4,5,6-Tetrachloro-7-(4-methoxyphenyl)bicyclo[2.2.2]oct-5-ene-2,3-dione (4). This MeOSty/oCA adduct was obtained via reaction of 270 μL (2.03 mmol) of *p*-methoxystyrene with 500 mg of *o*-chloranil in dichloromethane (yield 705 mg, 96%): mp 73−75 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (d, J = 10 Hz, 2H), 6.92 (d, J = 9 Hz, 2H), 3.80 (s, 3H), 3.53 (dd, J = 10.8, 5.1 Hz), 3.06 (dd, J = 14.4, 10.8 Hz, 1H), 2.82 (dd, J = 14.4, 5.4 Hz, 1H); FT-IR ν_{max} 2924, 1763, 1514, 1250, 826, 750 (cm^{-1}); UV−vis (CH_2Cl_2) λ_{max} = 444 nm, ε = 2.0 × 10^2 M^{-1} cm^{-1}. Anal. Calcd for $C_{15}H_{12}Cl_4O_3$: C, 47.40; H, 2.65. Found: C, 46.93; H, 2.93. X-ray structure of the product is presented in Figure 4, and the crystallographic data are provided the Supporting Information. Mixing of neat *p*-methoxystyrene with *o*-chloranil at 0 °C resulted in formation of a dark solid, which was stable at this temperature for several weeks.

To prepare a single crystal of the [MeOSty,oCA] complex, 270 μL (2.03 mmol) of *p*-methoxystyrene in 1 mL of dichloromethane was added (under a nitrogen atmosphere, at −78 °C) to the solution of 100 mg (0.4 mmol) of *o*-chloranil in 2 mL of dichloromethane in a Schlenk tube (50 mL). The resulting dark solution was carefully layered with ~2 mL of a 1:1 dichloromethane/hexane mixture, and then with 20 mL of hexane. Slow diffusion of hexane into the dichloromethane solution at −65 °C resulted in the formation of nearly black crystals of [MeOSty, oCA] suitable for single-crystal X-ray crystallography, together with the dark-red crystals of *o*-chloranil.

Spectral and Electrochemical Measurements. UV measurements were carried out using the quartz (1 mm path length) spectroscopic cell equipped with a Teflon valve fitted with Viton O-rings. A Dewar equipped with quartz lens was used for the measurements at −30 to −95 °C, and the temperature was adjusted with an ethanol-liquid nitrogen bath (±0.5 K). Formation constants and extinction coefficients were evaluated as described earlier.[33,51] Oxidation potentials of the styrene donors (Table S1 in the Supporting Information[52]) for Mulliken correlation were evaluated via cyclic voltammetry measurements. They were performed with a BAS 100A electrochemical analyzer equipped with a platinum electrode under an argon atmosphere with Bu_4PF_6 supporting electrolyte. The IR spectra of neat crystalline materials were recorded using single-reflection HATR.

X-ray Crystallography. Single crystals suitable for X-ray diffraction studies were mounted using oil on a glass fiber. All measurements were made on a APEX-II CCD using Mo Kα radiation (λ = 0.71073 Å) at 00(2) K. The structures were solved by direct methods and refined by full matrix least-squares treatment.[53]

Calculations. Reactants, products, and transition sates structures for the reaction between *o*-chloranil and styrenes were optimized at the B3LYP/6-311+G(dp) level using the Gaussian 03 program.[43] Vibrational frequencies have been calculated for all located stationary structures to verify whether they are minima or transition states. Each transition state had one and only one imaginary vibration frequency, and in each case, the vibrations associated with the imaginary frequency corresponded to the movement in the direction of the reaction coordinate. Zero-point energies (ZPE) and thermal corrections were taken from unscaled vibrational frequencies. Free energies and enthalpies are given at 25 °C. Solvent effects in dichloromethane have been taken in account by single-point calculations with the polarizable continuum model (PCM)[54] over the respective gas-phase geometries. The energy differences between exo- and endotransition states and charge-transfer complexes were evaluated via MP2/6-311+G(dp) single-point computations using the structures optimized via B3LYP/6-311+G(dp) method. The energies of the CT complexes, transition states, and products calculated relative to the corresponding reactants via MP2 method include basis set superposition error (BSSE) corrections (using the Boys−Bernardi counterpoise correction scheme),[55] as well as ZPE corrections and solvation from B3LYP computations. Atomic charges were calculated via natural population analysis (NPA) phase of natural bond orbital analysis.[56]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Redox potentials of donors and spectral characteristics of the CT complexes (Table S1); evaluation of charge transfer in the [MeOSty, oCA] complex (Table S2), energies of styrenes, CT complexes, TS, and products of the Diels−Alder reaction (Table S3); relative energies, enthalpies, and free energies (Table S4), energy diagram for the oCA/HSty pair (Scheme S1); the Cartesian coordinates of the calculated structures; temperature dependence of formation constant of the [MeOSty, oCA] complex (Figure S1); spectral changes during the MeOSty/oCA cycloaddition (Figure S2); kinetic curves for cycloaddition reactions (Figure S3); dependence of the rate of cycloaddition on the concentration of a donor and temperature dependence of rate constants (Figure S4); ORTEP diagrams of XSty/oCA adducts and hydrated cycloadducts (Figures S5 and S6); NMR spectra of cycloadducts (Figure S7); molecular orbital shapes (Figure S8); calculated structures of HSty/oCA associates (Figure S9); ESP (Figure S10); CIF files for the [MeOSty, oCA] complex and XSty/oCA cycloadducts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon: Oxford, 1990.

(2) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G.; Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668−1698.

(3) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie International: Deerfield Beach, FL, 1970.

(4) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Book: Sausalito, CA, 2006.

(5) Epiotis, N. D. *J. Am. Chem. Soc.* **1972**, *94*, 1924−1934.

(6) Thompson, C. C.; Holder, D. D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 257−262.

(7) Kiselev, V. D.; Miller, L. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036−4039.

(8) Houk, K. N.; Rondan, N. G.; Mareda, J. *Tetrahedron* **1985**, *41*, 1555−1563.

(9) Kim, E.; Christi, M.; Kochi, J. K. *Chem. Ber.* **1990**, *123*, 1209−1218.

(10) Klemm, L. H.; Solomon, W. C.; Tamiz, A. P. *J. Org. Chem.* **1998**, *63*, 6503−6510.

(11) Bachrach, S. M.; Jiang, S. *J. Org. Chem.* **1999**, *64*, 8248−8255.

(12) Wise, K. E.; Wheeler, R. A. *J. Phys. Chem. A* **1999**, *103*, 8279−8287.

(13) Handoo, K. L.; Lu, Y.; Parker, V. D. *J. Am. Chem. Soc.* **2003**, *125*, 9381−9387.

(14) Jones, G. O.; Guner, V. A.; Houk, K. N. *J. Phys. Chem. A* **2006**, *110*, 1216−1224.

(15) Berionni, G.; Bertelle, P.-A.; Marrot, J.; Goumont, R. *J. Am. Chem. Soc.* **2008**, *131*, 18224−18225.

(16) Rosokha, S. V.; Kochi, J. K. *J. Org. Chem.* **2002**, *67*, 1727−1737.

(17) Scheiner, S., Ed. *Molecular Interaction. From van der Waals to Strongly Bound Complexes*; Wiley: New York, 1997.

(18) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1111.

(19) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 6284−6289.

(20) Sustmann, R.; Dern, M..; Kasten, R.; Sicking, W. *Chem. Ber.* **1987**, *120*, 1315−1322.

(21) Sustmann, R.; Korth, H. G.; Nuchter, U.; Siangouri-Fuelner, I.; Sicking, W. *Chem. Ber.* **1991**, *124*, 2811−2817.

(22) Fukuzumi, S.; Kochi, J. K. *Tetrahedron* **1982**, *38*, 1035−1049.

(23) Lotri, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2131−2136.

(24) Uosaki, Y.; Nakahara, M.; Osugi, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2569−2572.

(25) Uosaki, Y.; Nakahara, M.; Osugi, J. *Int. J. Chem. Kinet.* **1982**, *14*, 985−996.

(26) Herbstein, F. H. *Crystalline Molecular Complexes and Compounds. Structure and Principles*; Oxford University Press: Oxford, UK, 2005.

(27) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(28) Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969.

(29) Kim, J. H.; Linderman, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 4951−4959.

(30) Homer, L.; Merz, H. *Justus Liebigs Ann. Chem.* **1950**, *570*, 89−120.

(31) Burnell, R. H.; Taylor, W. I. *J. Chem. Soc.* **1954**, 3936−3937.

(32) Schonberg, A.; Latif, N.; Moubasher, R.; Sina, A. *J. Chem. Soc.* **1951**, 1364−1368.

(33) Rosokha, S. V.; Dibrov, S. M.; Rosokha, T. Y.; Kochi, J. K. *Photochem. Photobiol. Sci.* **2006**, *5*, 914−924.

(34) It should be noted, however, that tetrathiafulvalene is a very strong donor, which is characterized by the oxidation potential of 0.37 V vs SCE. Accordingly, its reaction with *o*-chloranil acceptor (E_{red}^{o} = 0.15 V vs SCE) proceeds via electron-transfer mechanism in which a CT complex facilitates formation of the ion radical pair which collapses into the heterocycloadduct.[33] In comparison, styrenes are much weaker donors (vide infra) and electron-transfer processes are less likely to play a significant role in their reactions with oCA.

(35) Subtraction of the absorbancies of the components from the absorption of the solutions containing oCA/MeOSty revealed appearance of two new bands in the visible range, one with maximum in the 450−600 nm range (vide infra) and another with maximum in the 350−450 nm range (similar two bands were observed in the solutions with the other styrenes, as well). Like with other donor/acceptor associates,[28] these bands are most likely related to the charge transfer from HOMO and HOMO-1 of the donor to the acceptor's LUMO.

(36) Drago, R. S. *Physical Methods in Chemistry*; Saunders Co.: Philadelphia, PA, 1977.

(37) Overlap of the absorption bands of [oCA,XSty] complexes (X = H, Cl, or Me) with absorption band of oCA acceptor hindered accurate evaluation of the thermodynamic parameters Δ*H* and Δ*S* for the corresponding equilibria.

(38) The angle between oCA and MeOSty planes is 2.54°. Therefore, the interpalnar separation of ∼3.20 Å was determined as average distance between oCA atoms and a mean MeOSty plane.

(39) The absence of the X-ray structural data for the separate neutral donor and its cation radical hinders evaluation of the charge transfer in the [MeOSty, oCA] complex based on the structure of the MeOSty moiety. The structural comparison of this moiety with the neutral molecule intercalated in the tetraarylporphyrin-based clathrate[40] and with the cation radical obtained via DFT B3LYP/6-311G calculations resulted in the value of charge transfer of 0.26 (Table S2). When large variation of the values calculated using particular bond length was taken into account, this number is consistent with that obtained from the analysis of oCA structure.

(40) Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Terzis, A.; Strouse, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 9480−9497.

(41) The measurements of absorbance vs time dependencies at different wavelength resulted, within the accuracy of experiments, in the same values of rate constants. Note that the detailed results of the kinetics of the cycloaddition in the oCA/XSty systems will be reported separately.

(42) The reactions between oCA acceptor and various styrene donors under air at room temperature resulted in formation of the white crystalline products. X-ray measurements of the single crystals taken from these systems revealed that these products are hydrated dihydroxycyclohexanone cycloadducts (see Figure S6 in the Supporting Information). Furthermore, yellow products of XSty/oCA cycloaddition were also moisture-sensitive, and they gradually turned white when stored under air. Formation of the hydrated product was also reported by Homer and Merz.[30]

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.

(44) Similar trend was observed in the Diels−Alder reaction of *o*-fluoranil. See: Lemal, D. M.; Sang, D.; Ramanathan, S. *J. Org. Chem.* **2009**, *74*, 7804.

(45) Wannere, C. S.; Paul, A.; Herges, R.; Houk, K. N.; Schaefer, H. F.; Schleyer, P. v. R. *J. Comput. Chem.* **2006**, *28*, 344−361.

(46) (a) At −35 °C, the ratio of the rate constants may be estimated as $k_{endo}/k_{exo} = \exp(-\Delta\Delta E/RT) = \exp(2300 \text{ cal mol}^{-1}/(238 \text{ K} \times 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}) \approx 130$. (b) Note that X-ray structural analysis of the crystalline white product resulting from the reaction between MeOSty donor and oCA acceptor at room temperature under air revealed hydrated cycloaddition product in exo-configuration (Figure S6). It indicates that a significant amount of the exoadduct forms at higher temperatures; that is, the difference of the energies of transition state leading to exo- and endoisomers is not very high.

(47) It is noticeable that the activation enthalpies calculated at B3LYP level (18.0 and 16.0 kcal/mol for the endo-TS for the oCA/HSty and oCA/MeOSty reactions, respectively) are higher than the experimental values (11.0 and 8.4 kcal/mol for the oCA/HSty and oCA/MeOSty reactions, respectively). In comparison, the enthalpies obtained from the MP2 computations (∼1 kcal/mol for both pairs) are lower than those obtained from the experiments. These deviations are consistent with the earlier analysis of the performance of different computational methods for calculations of transition-state energies, in particular, those for the Diels−Alder reactions.[57] They revealed that calculations with B3LYP functional usually overestimate barrier heights (due to underestimation of dispersion components), while the MP2 computations underestimate such barriers. However, the combination of MP2 and B3LYP computations with the 6-311+G(dp) basis set was a method of choice for the scrutiny of the relative energies of the transition states leading to the endo- and exoisomers.[45] In our systems, both DFT and MP2 methods produced lower energies of the endo-TS as compared to their exoanalogues (see Table S4 in the Supporting Information), and the calculated at MP2 level differences of ∼2.5 kcal/mol are consistent with the experimental characterization of the products obtained at low and room temperatures. On the other hand, the quantitative analysis of the kinetics of the Diels−Alder reactions involving various XSty/oCA pairs (which require more precise evaluation of the absolute energies of the barriers using dispersion-corrected functionals[57]) is beyond the scope of the current work and will be presented separately.

(48) UV−vis spectral measurements indicate that in dichloromethane solutions with concentrations of oCA acceptor and XSty donor of ∼10 mM each at room temperature the concentration of complex is less than 0.1 mM.

(49) Since the stability of CT complexes generally rises with the increase of donor strength in the series of related systems, the different behavior of such mixtures may be also related to the fact that [Sty, oCA], [ClSty, oCA], and [MeSty, oCA] complexes are more labile.

(50) See, for example, computations of the anthracene/tetracyanoethylene pair by Wise and Wheeler.[7]

(51) Ganesan, V.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 2559−2571.

(52) Owing to the high reactivity of the oxidized styrenes, their reversible redox potentials were not accessible. Thus, we used the irreversible anodic waves for the evaluation of their donor strength. Although these waves are affected by kinetic terms, the oxidation potentials measured for different donors under the same conditions reasonably reflected the change of their relative values (although they deviated from strict thermodynamic characteristics) and may be used in the various correlations.[22,33]

(53) Sheldrick, G. M. *SHELXTL*, version 6.14; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003.

(54) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3093.

(55) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553−566.

(56) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(57) (a) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936−2941. (b) Ess, D. H.; Houk, K. N. *J. Phys. Chem. A* **2005**, *109*, 9542−9553. (c) Lan, Y.; Zou, L. F.; Cao, Y.; Houk, K. N. *J. Phys. Chem. A* **2011**, *115*, 13906−13920. (d) Xu, X. F.; Alecu, I. M.; Truhlar, D. G. *J. Chem. Theory Comput.* **2011**, *7*, 1667−1676.