Charge-Transfer Complexes of Thiopyrylium Cation with Aromatic Hydrocarbons and Olefins

Zen-ichi Yoshida,* Toyonari Sugimoto, and Shigeo Yoneda
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606

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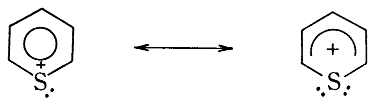
Charge-transfer (CT) interaction of the thiopyrylium cation (**1**) with aromatic hydrocarbons and olefins has been investigated by electronic spectroscopy. It is noteworthy that **1** formed a CT complex with a monoolefin. The observed CT spectra in the **1**–olefin system showed the following remarkable contrasts compared with those in the **1**–aromatic system. 1) Although one CT absorption band was observed for the **1**–aromatic hydrocarbon CT complex, while two CT absorption bands for the 1–olefin CT complex, and 2) the value of a in the equation of $\Delta E_{CT}=aIP_D+b$ was 1.04 for the former complex and 0.27 for the latter complex. A detailed discussion on the difference between the two CT complexes is presented.

Thiopyrylium cation (**1**)[1] belongs to a novel class of heterocyclic system. The question whether this system is represented by the dominant cyclic 6π aromatic structure (**1a**) or it is more accurately represented as a hybrid structure principally composed of sulfur-bridged carbonium ion structure (**1b**) is intriguing from organic as well as physicochemical view points.



1a   **1b**

Our studies on the interpretation of its electronic spectrum[2] by the SCF-MO method and on its reactions with nucleophiles[3] indicated that **1** can be regarded as the carbonium ion stabilized by the (2p-3p)π conjugation with the sulfur atom. In the reactions of **1** with carbanions and amines, we expected that the reaction might proceed *via* a CT complex between **1** and the nucleophile. However, for both **1**–carbanion and **1**–amine systems such CT complex formation has not been observed by spectroscopic means because the reaction between **1** and the nucleophile with low ionization potential occurs very rapidly. This situation prompted us to investigate the CT complex formation between **1** and aromatic hydrocarbons or olefins which have higher ionization potentials than carbanions and amines. Interestingly, we observed the **1**–monoolefin CT complexes[4] as well as the **1**–aromatic hydrocarbon CT complexes, and found that **1** behaves as a strikingly different π electron acceptor from tetracyanoethylene[5] and 1,3,5-trinitrobenzene[6] in the CT complex formation with aromatic hydrocarbons and olefins. In this paper we report investigation on such an interesting CT interaction of **1** with aromatic hydrocarbon and monoolefin, and discuss difference between the two CT complexes.

Experimental

Thiopyrylium perchlorate was prepared according to the method of Degani *et al.*[1c] and purified by reprecipitation from acetonitrile–ether.

Aromatic hydrocarbons and olefins used were purified before use in the following manners. *m*-Xylene, mesitylene, 1-methylnaphthalene and 2-methylnaphthalene were purified by distillation *in vacuo*. Naphthalene, pyrene and anthracene were purified by sublimation under reduced pressure. Cyclohexene, 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, 1-pentene, ethyl vinyl ether and *n*-butyl vinyl ether were purified by distillation *in vacuo*. Acetonitrile was dried over phosphorus pentoxide, repeatedly distilled, treated with anhydrous potassium carbonate and finally distilled without a drying agent.

The electronic spectra were recorded on a Hitachi EPS-3T type spectrophotometer at room temperature.

The pK_{R^+} value for the 1-ethylpyridinium cation was estimated from a determination of the pH of aqueous solutions of the perchlorate salt.

Results and Discussion

CT Complexes between the Thiopyrylium Cation 1 and Aromatic Hydrocarbons. A new absorption band was observed in the ultraviolet or visible region for the mixed solution of **1** and an aromatic hydrocarbon in acetonitrile, which is due to neither **1** nor an aromatic hydrocarbon. For example, the absorption spectrum of the **1**–mesitylene system reveals a new band at 345 nm as shown in Fig. 1. The maximum wavelengths of new bands observed for the **1**–aromatic hydrocarbon system are listed in Table 1. When the maximum

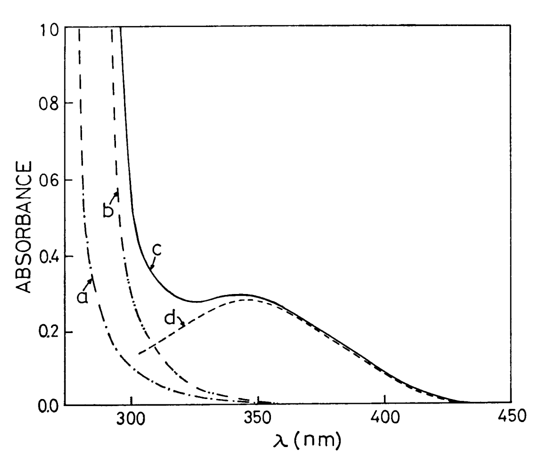


Fig. 1. Absorption spectra in acetonitrile: (a) Thiopyrylium perchlorate (1.3×10^{-3} mol/l) (b) Mesitylene (0.3 mol/l) (c) Thiopyrylium perchlorate (1.3×10^{-3} mol/l) and mesitylene (0.3 mol/l) (d) The calculated absorption for the thiopyrylium perchlorate–mesitylene CT complex.

Table 1. CT absorption bands of the **1**[a] -aromatic hydrocarbon complexes in acetonitrile

Donor[b]	$\lambda_{\max}$ (nm)	*IP* (eV)
m-Xylene	319	8.56[c]
Mesitylene	345	8.39[c]
Naphthalene	383	8.12[c]
2-Methylnaphthalene	396	8.03[c]
1-Methylnaphthalene	405	7.96[c]
Pyrene	462	7.55[d]
Anthracene	467	7.37[d]

a) A concentration of 1.3×10^{-3} mol/l. b) A concentration in the 0.1—0.5 mol/l range. c) K. Watanabe, *J. Chem. Phys.*, **26**,, 542 (1957). d) J. B. Birks and M. A. Slifkin, *Nature*, **191**, 761 (1961).

transition energies (ΔE_{CT}) of the new bands are plotted against the ionization potentials (IP_D) of aromatic hydrocarbons, a straight line with slope close to unity is obtained (Fig. 2). This demonstrates that the new bands are due to the CT complexes between **1** and aromatic hydrocarbons.

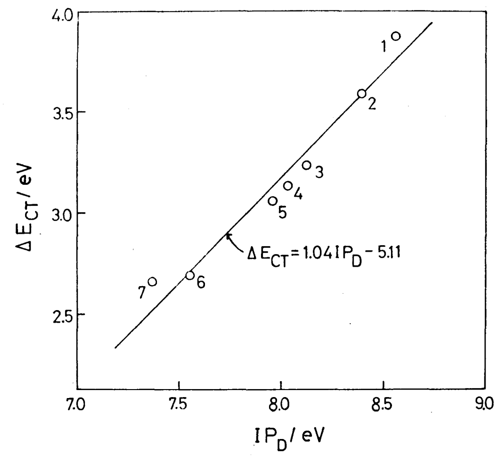


Fig. 2. Plot of the CT transition energies (ΔE_{CT}) *vs.* the ionization potentials (IP_D) of aromatic hydrocarbons: (1) *m*-Xylene, (2) Mesitylene, (3) Naphthalene, (4) 2-Methylnaphthalene, (5) 1-Methylnaphthalene, (6) Pyrene, and (7) Anthracene.

The equilibrium constant and the extinction coefficient for the **1**-mesitylene CT complex were determined to be 0.16 l·mol^{-1} and 2900 at 20.0°C, respectively, by the Benesi-Hildebrand equation.[7] Feldman and Winstein have observed the similar phenomenon for the tropylium perchlorate (**2**)-aromatic hydrocarbon system in acetonitrile and obtained the equilibrium constant of 0.67 l·mol^{-1} (25.0°C) and the extinction coefficient of 1850 for the 1 : 1 CT complex between **2** and mesitylene.[2,8] The value of the equilibrium constant obtained for the **1**-mesitylene CT complex is much smaller than that for the **2**-mesitylene CT complex. In contrast with these cations, the 1-ethylpyridinium cation (**3**) did not exhibit CT absorptions with aromatic hydrocarbons. This clearly indicates that abilities of their cations as electron acceptors in the CT complex formation decrease in the order of tropylium>thiopyrylium>pyridinium cations. This tendency is coincident with the reverse order of the pK_{R^+} values for their cations (**2**, +4.7;[9] **1**, +8.7;[10] **3**, +11.5). The contribution of the carbonium ion structure to the cations is closely related to their electron accepting ability in the CT complex formation.

*CT Complexes between **1** and Olefins.* When olefins are employed in place of aromatic hydrocarbons as an electron donor, two CT bands are observed in the ultraviolet and visible regions.[11] As one example the CT absorption spectrum of the **1**-cyclohexene system is shown in Fig. 3. The maximum wavelength of the two CT bands observed for the **1**-olefin system are listed in Table 2. Figure 4 shows that the plots of the transition energies (ΔE_{CT}) of the first (I) and the second (II) CT bands *vs.* the ionization potentials (IP_D) of olefins give straight lines with the same slope (0.27) whose value is significantly small compared with that (1.04) for the **1**-aromatic hydrocarbon CT complexes (see Fig. 2). The two absorption bands observed for the **1**-olefin system are attributed to those due to the CT complex formation between **1** and olefin.

The equilibrium constant and the extinction coefficient for the **1**-cyclohexene CT complex were determined to be 2.00 l·mol^{-1} and 185, respectively.

Multiple CT bands in donor-acceptor complexes

Table 2. CT absorption bands of the **1**[a] -olefin complexes in acetonitrile

Donor[b]	$\lambda_{\max}$ (nm) Second CT band[c] (II)	$\lambda_{\max}$ (nm) First CT band (I)	*IP* (eV)
1-Pentene	—[d]	406	9.67[f]
Isobutene	310	420	9.26[f]
Cyclohexene	311	422	9.18[f]
1-Methylcyclohexene	311	422	
3-Methylcyclohexene	311	422	
4-Methylcyclohexene	311	—[e]	
Ethyl vinyl ether	315 (sh)	434	8.93[f]
n-Butyl vinyl ether	315 (sh)	434	

a) A concentration of 1.3×10^{-3} mol/l. b) A concentration in the 0.1—0.3 mol range. c) Thiopyrylium perchlorate itself has the absorptions at 246 nm (log ε=3.74) and 284 (3.55) in acetonitrile. The second CT bands are found by the usual procedure dissolving the component molecules. d) Exact analysis between 284 nm band of thiopyrylium perchlorate and the second CT band is difficult. e) The spectrum in this region can not be analyzed, because the absorption band of the reaction product overlaps with the first CT band of the system. f) J. Collins and F. P. Lossing, *J. Amer. Chem. Soc.*, **81**, 2064 (1959).

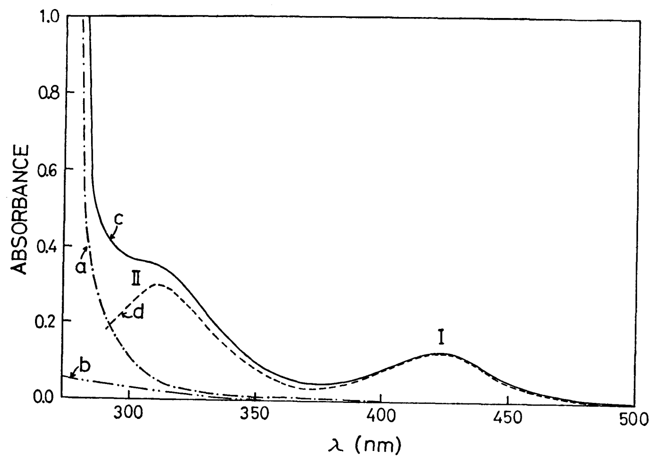


Fig. 3. Absorption spectra in acetonitrile: (a) Thiopyrylium perchlorate (1.3×10^{-3} mol/l) (b) Cyclohexene (0.3 mol/l) (c) Thiopyrylium perchlorate (1.3×10^{-3} mol/l) and cyclohexene (0.3 mol/l) (d) The calculated absorption for the thiopyrylium perchlorate-cyclohexene CT complex. The bands, I and II, correspond to the first and the second CT absorption bands, respectively.

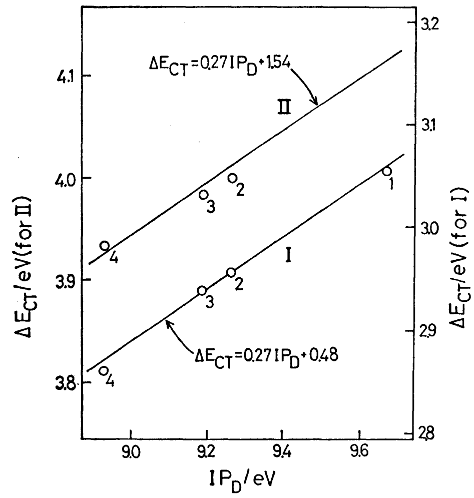


Fig. 4. Plots of the CT transition energies (ΔE_{CT}) of the first (I) and the second (II) CT absorption bands *vs.* the ionization potentials (IP_D) of olefins: (1) 1-Pentene, (2) Isobutene, (3) Cyclohexene and (4) Ethyl vinyl ether.

have been assigned to electronic transitions from two upper occupied levels in the donor[12] or to two lower unoccupied levels in the acceptor.[1,13] In the case of 1-methylpyridinium iodide[14] and 2,4,6-trimethylpyrylium iodide[15] two CT bands were once assigned to the formation of $^2P_{3/2}$ and $^2P_{1/2}$ iodine atoms in the excited state, on the basis that the separation between the two bands corresponded nearly to that expected for the formation of iodine atom in two states.[16] However, recent experimental results have indicated that the two CT bands observed in 1-methylpyridinium iodide are in fact due to the electronic transitions from the highest occupied MO of the iodide anion to the lowest and the second unoccupied π-MO's of the pyridinium cation.[17-19] Verhoeven, Dirkx and de Boer have investigated the CT interaction between the *N*-methyl-4-cyanopyridinium ions and aromatic hydrocarbons, and also observed the two CT bands which are caused by the presence of two closely located unoccupied MO's in the pyridinium cation.[20] In the case of the **1**-olefin CT complexes, the two CT bands should be assigned to the electronic transitions from the highest occupied π-MO of olefin to the lowest and the second unoccupied π-MO's of **1** as visualized in Fig. 5, since olefin has only one occupied π-MO. From Fig. 4, the energy difference between the first and the second CT bands is almost constant independent of olefins employed and 1.06 eV. Furthermore, the observed energy difference is very close to the calculated energy difference between the lowest and the second unoccupied π-MO's of **1** by the SCF-MO method;[2] *i. e.*, 1.065 eV. The above mentioned facts lead to the conclusion that the two closely located unoccupied π-MO's of **1** play an important role in the appearance of the two CT bands for the case of the olefin complexes.

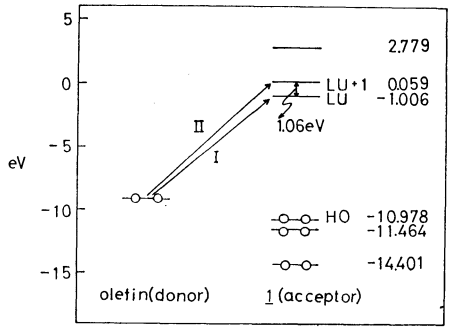


Fig. 5. Energy diagram for the **1**-olefin CT complex. I and II correspond to the first and the second CT absorption bands, respectively.

We can suggest the geometry of the **1**-olefin CT complex considering the "overlap and orientation principle."[21] The overlap between the orbitals of two component molecules will determine the resonance capability of the CT-bond and the nobond structures; that is, the relative positions of **1** and olefin molecules in the CT complex will be such as to make possible overlaps of the highest occupied π-MO of olefin with the lowest and the second unoccupied π-MO's of **1** (see Fig. 6). From Fig. 6 we can immediately illustrate only one possible configuration shown in Fig. 7 as the geometrical structure of the **1**-olefin CT complex, where olefin is located on the α-carbons of **1**. The SCF-MO calculation indicates that in this configuration the highest occupied MO of olefin overlaps more effectively with the (LU+1)MO than with the LUMO of **1**, consistent with the observation that the higher energy

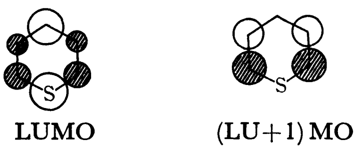


Fig. 6. The lowest unoccupied (LU) and the second unoccupied (LU+1) MO's of **1** calculated by the SCF-MO method.

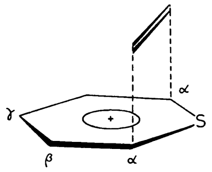


Fig. 7. Geometrical configuration for **1**-olefin CT complex.

CT band is more intense than the lower energy one (see Fig. 3).

*Comparison between the **1**-Aromatic Hydrocarbon and the **1**-Olefin CT Complexes.* The **1**-aromatic hydrocarbon and the **1**-olefin CT complexes have the folowing marked differences: (1) only one CT band is observed for the former,[22] while two CT bands for the later, and (2) the slope obtained by the plot of the CT transition energies *vs.* the ionization potentials of donors is 1.04 for the aromatic hydrocarbon complexes and 0.27 for the olefin complexes.

According to Mulliken's CT treatment of the electron donor-acceptor complexes,[23] their CT transition energy (ΔE_{CT}) depends upon the donor ionization potential (IP_{D}) and the acceptor electron affinity (EA_{A}) as expressed in Eq. (1):

$$\Delta E_{\mathrm{CT}} = IP_{\mathrm{D}} - EA_{\mathrm{A}} + C_1 + \frac{C_2}{IP_{\mathrm{D}} - EA_{\mathrm{A}} + C_1} \quad (1)$$

The energy term C_1 mainly comprises the difference between the Coulomb attraction D$^+$-A$^-$ after excitation and the van der Waals bonding energy D···A before excitation; C_2 reflects intermolecular resonance. If CT interaction is weak, the fourth term in Eq. (1) will vanish because C_2 is considered to be nearly zero. Actually, the following equation (Eq. (2))* was obtained in the **1**-aromatic hydrocarbon (IP_{D}=7.37—8.56 eV) complexes as shown in Fig. (2). On the other hand, in the case of **1**-olefin (IP_{D}=8.93—9.67 eV) CT

$$\Delta E_{\mathrm{CT}} = 1.04 IP_{\mathrm{D}} - 5.11 \quad (2)$$

complexes, Eqs. (3) and (4) were empirically obtained from Fig. 4 for the first and second CT absorption bands, respectively, since the C_2 term is considerably large, indicating that olefins more strongly interact with **1**.

$$\Delta E_{\mathrm{CT}} = 0.27 IP_{\mathrm{D}} + 0.48 \quad (3)$$

$$\Delta E_{\mathrm{CT}} = 0.27 IP_{\mathrm{D}} + 1.54 \quad (4)$$

This is also supported by the fact that the **1**-cyclohexene CT complex has a large equilibrium constant (2.00) compared with the **1**-mesitylene CT complex (0.16). Thus appearance of two CT bands in the **1**-olefin CT complexes is considered to be due to strong interaction between them.

It is well known that generally π electron acceptors such as tetracyanoethylene[5] and 1,3,5-trinitrobenzene[6] form stronger CT complexes with aromatic hydrocarbons than with olefins. In marked contrast with the usual case, it is interesting that **1** forms stronger CT complex with olefin than with aromatic hydrocarbon. This is the first case in π-π type CT complexes.

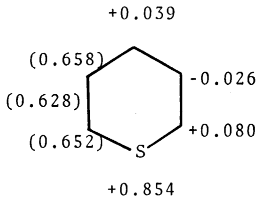


Fig. 8. Positive charge distribution and π-bond orders of **1** calculated by the SCF-MO method.

The strong CT interaction of **1** with olefin is due to the characteristic nature of **1**. It has already been suggested that the possible geometry for the **1**-olefin CT complex is one of olefin locating itself on the α-carbons of **1** (see Fig. 7), on which the positive charge localizes most as seen in the positive charge distribution calculated by the SCF-MO method[2] (Fig. 8). This geometry supplies a condition for the strong CT interaction between **1** and olefin, in which the unoccupied α-carbon 2p π-MO's of **1** overlap effectively with the occupied 2p π-MO's of olefin.

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* Under the assumption that C_1, C_2 and EA_{A} are constants for comparable CT complexes between the same electron acceptor and different electron donors of high ionization potentials,[24] Eq. (1) canbe replaced by linear expression as follows:[25]

$$\Delta E_{\mathrm{CT}} = aIP_{\mathrm{D}} + b$$

In a weak CT interaction, the value of a is nearly equal to unity because the C_2 term is nearly zero. Whereas, in a stronger CT interaction the values of a becomes smaller than unity because C_2 is not zero.

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