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THIOPYRYLIUM ION AS AN ELECTRON ACCEPTOR IN CHARGE-TRANSFER COMPLEX FORMATION

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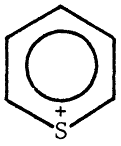
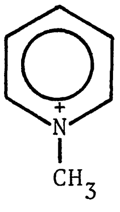
Thiopyrylium ion (I) has been found to form the CT complex having two CT absorption bands with olefin. Appearance of the two CT bands is rationalized by the existence of two closely located vacant orbitals of I.

We have carried out the extensive works on the reactions of thiopyrylium ion (I) with nucleophiles (amines and carbanions from active methylene compounds),[1] which seemed to proceed via a charge-transfer complex between both the reactants. However, for I- amine or I- stabilized carbanion system we could not spectroscopically observe the CT complex formation, because the reaction took place rapidly. On the other hand, I (6π system) has a formal structure replaced -CH= group of benzene with $-\overset{+}{S}=$. It is well known that benzene acts as a π-donor and does not behave as a π-acceptor in the formation of CT complexes. We were interested by the CT complexes involving I in these circumstances.

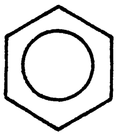
Although N-methylpyridinium ion (II) isoelectronic to I and benzene (III) didn't form CT complexes with olefins, I has been found to form CT complexes with olefins. It is interesting that the two CT absorption bands in ultraviolet and visible regions were observed for the I-olefin system.



I



II



III

$$\mathrm{I} + \text{Olefin} \longrightarrow \text{CT complex}$$

$$\mathrm{II} + \text{Olefin} \not\longrightarrow \text{CT complex}$$

$$\mathrm{III} + \text{Olefin} \not\longrightarrow \text{CT complex}$$

Kosower has observed the two CT absorption bands for the II-iodide anion system and interpreted them as the electronic transitions from the highest and the second highest occupied levels of the iodide anion to the lowest vacant level of II.[2] However, such an interpretation is not applicable for our case, because olefin has only one occupied molecular orbital. The alternative is that the two CT absorption bands are due to the electronic transitions from the highest occupied level of olefin to the lowest and the second lowest vacant levels of I.

The ultraviolet and visible absorption spectra of the I-olefin system in acetonitrile have been measured by the usual method. As the counter ion of I, the perchlorate anion has been chosen which does not form the CT complex with I. The observed two new bands were assigned to the CT absorption bands[3] from the following reasons: Since the frequencies of the CT absorption bands for a series of donors with any one acceptor change nearly linearly with the ionization potentials of the donors, straight lines should be expected for the plots of the frequencies of the CT absorption bands vs. the ionization potentials of the donors.[4] In fact, the plots of the frequencies of the first and the second absorption bands vs. the ionization potentials[5] of olefins show linear relationships with the same positive slope, respectively, as is seen in Figure 1. As one example, the equilibrium constant for the I-cyclohexene system has been determined. With cyclohexene concentration in the 0.1-0.3 M range and thiopyrylium perchlorate concentration of 1.0×10^{-3} M in acetonitrile, Benesi-Hildebrand[6] and Ketelaar[7] plots of the observed absorbance at 422 mμ (first CT band), assuming 1:1 complex formation, have given good linear relationships, respectively. From the intercepts and slopes of these straight lines, it has been determined using the least square method that the equilibrium constant is 2.00 ± 0.05 $\mathrm{l.mole^{-1}}$ at 26.5 ± 0.5° and the extinction coefficient of the first CT band is 185. Appearance of the two CT absorption bands is rationalized by the existence of the two closely located vacant orbitals of I, as is visualized in Figure 2.

The value of the energy difference between the two CT absorption bands is given to be 1.06 eV from Figure 1. On the other hand, the SCF calculation[8] gives the value of 1.065 eV as the energy difference between the lowest and the second lowest vacant orbitals of I, which is in quite good agreement with the observed value. Since the value of the energy difference between the highest occupied and the second highest occupied orbitals of I is 0.486 eV, the reverse type of the CT complex formation is excluded. Therefore, it is

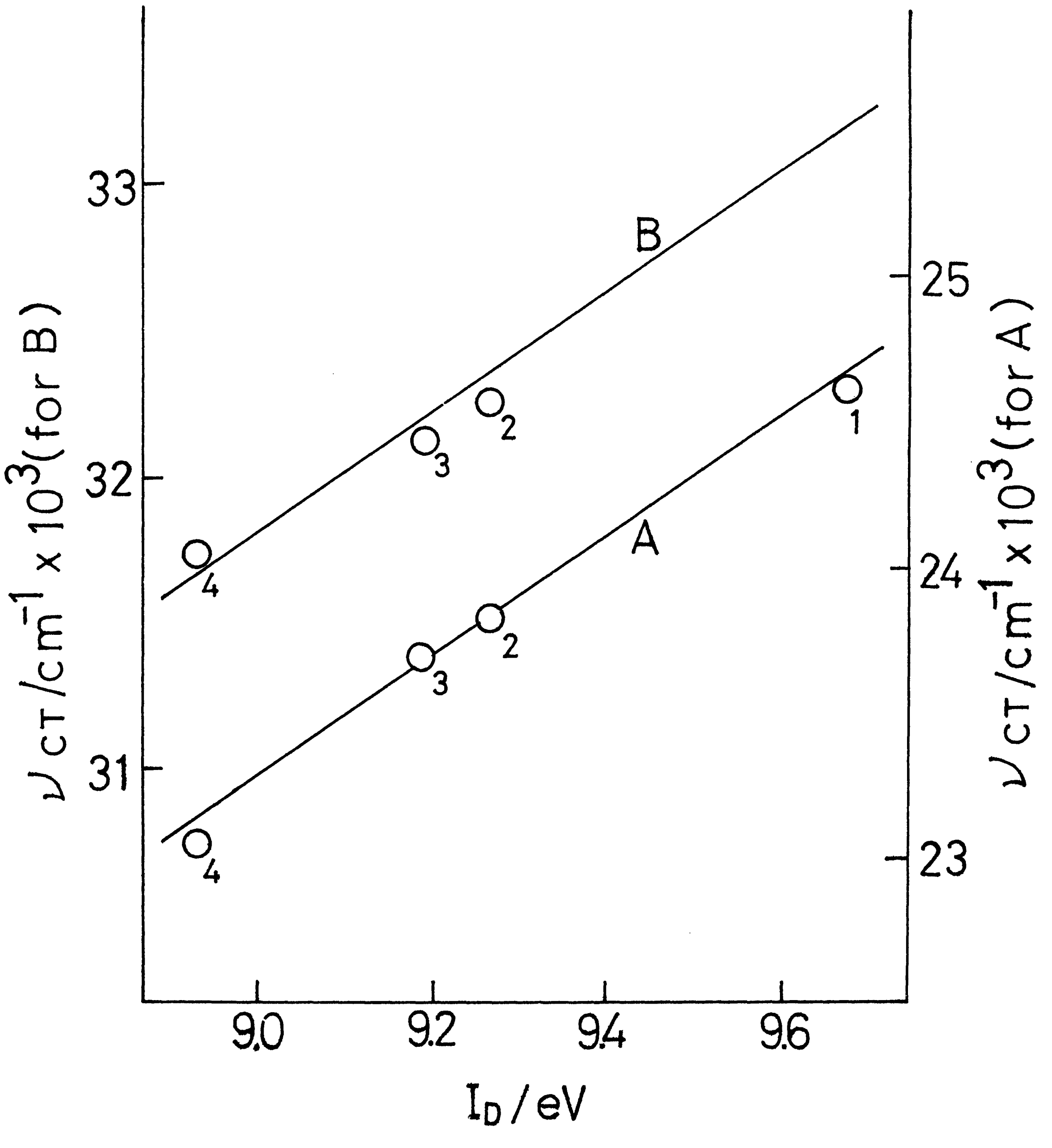


Figure 1. Plots of the frequencies (ν_{CT}) of the first (A) and the second (B) CT absorption bands vs. the ionization potentials (I_D) of olefins:
1:1-Pentene, 2: Isobutene, 3: Cyclohexene,
4: Ethylvinyl ether

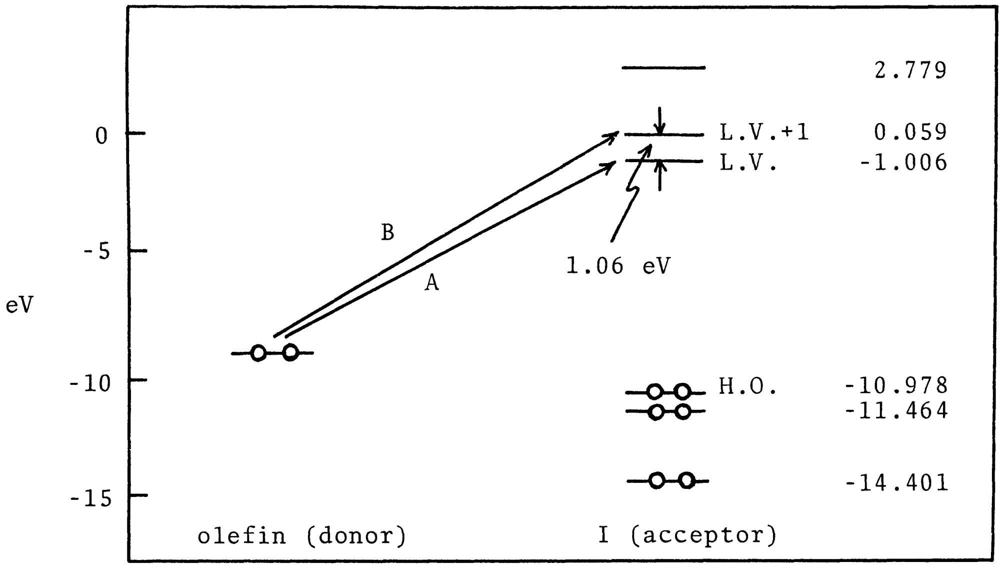


Figure 2. Energy diagram for the I-olefin CT complex. I and II correspond to the first and the second CT absorption bands, respectively.

concluded that I acts as a π-acceptor and the two CT absorption bands observed for the I-olefin system are due to the electronic transitions from the highest occupied level of olefin to the lowest and the second lowest vacant levels of I.

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