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Do Phosphonium And Sulfonium Cyclopentadienylides Have Ylide Structure or Ylene Structure ?

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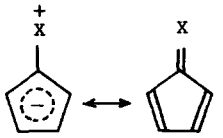
Preparations and interesting reactions of many phosphonium and sulfonium ylides have been reported so far.[1] However, an ambiguity has been seen for the ground state structure of these ylide compounds. The ground state structures of such compounds have been represented by both "dipolar ylide" ($\overset{-}{C}\text{-}\overset{+}{X}$) and "covalent ylene" (C=X) structures, or by ylide-ylene resonance structures.[1] For instance, Ramirez and Levy[2] have suggested roughly equal contributions of ylide and ylene structures to the triphenyl phosphonium cyclopentadienylide, the observed moment (7.0 D) corresponding to the middle value between the calculated π-moment of ylide structure (14.0 D) and that of ylene structure (nearly zero). However, the values of their calculated moment are incorrect, because they didn't take in account the σ-moment (opposite direction to π-moment). These situations prompted us to determine the exact contributions of the both structures for phosphonium and sulfonium cyclopentadienylides. Since for such complicated systems the dipole moment method seems to give an unreliable result, the electronic spectra of cyclopentadienylides and "molecules in molecule method" (semi-empirical MO method)[3] have been combined as a new method. As the phosphonium cyclopentadienylide, tri-n-propylphosphonium cyclopentadienylide (I), a new compound, was synthesized by the known method,[2] and recrystallized from n-hexane and sublimated at 60° (0.01 mmHg), m.p. 67.8-69.5°. nmr spectrum showed two multiplets at τ 3.63-3.75 (cyclopentadienylide ring hydrogen, 4H) and at τ 7.7-9.1 (n-propyl hydrogen, 21H).



ylide ylene

($\overset{+}{X}$: $-\overset{+}{P}\lessdot$ or $-\overset{+}{S}\lessdot$)

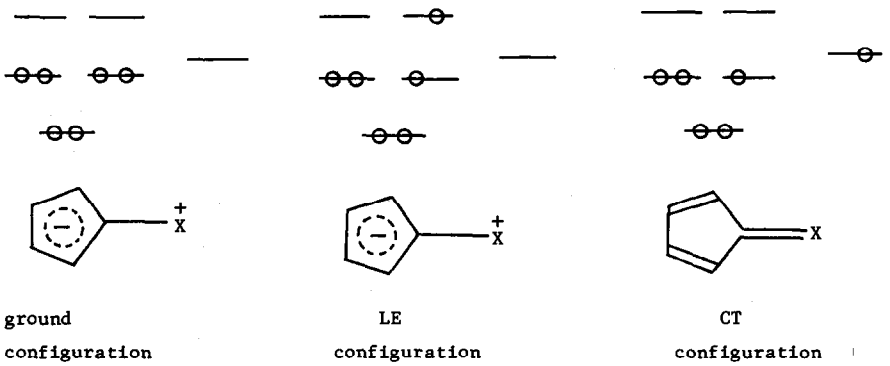
As sulfonium cyclopentadienylide, dimethylsulfonium cyclopentadienylide (II) was prepared according to Behringer and Scheidl[4] and purified by sublimation at 80° (0.002 mmHg). m.p. 129.5-130°. The electronic spectra of (I) and (II) in non-polar and polar solvents have been shown in Table 1. As is seen in Table 1, A band has shifted to shorter wave length by changing a solvent from n-hexane to methanol suggesting that A band is an intramolecular

Table 1 Electronic Spectra (λ_{max} in mμ and ϵ_{max}) of I and II

Solvent	I		II	
	A band	B band	A band	B band
Hexane	268 (1.3×10^4)	196 (1.6×10^4)	294 (1.3×10^4)	195 (1.5×10^4)
Methanol	254 (1.2×10^4)	198 (1.6×10^4)	273 (1.2×10^4)	195 (1.5×10^4)

charge-transfer (CT) band, it may be interpreted that the ground state should be more stabilized in methanol (polar) than in n-hexane (nonpolar), and the CT excited state should not be affected by methanol or by n-hexane. On the other hand, B-band might be interpreted as a locally excited (LE) band, this band being rather insensitive to changing solvent.

The transition energies of (I) and (II) have been calculated by "molecules in molecule method" assuming that the molecule (DX) is composed of an electron donating group (five-membered ring, D) and an electron accepting group (heteroatom, X). To understand the ground and CT excited states of DX, it is necessary to consider the interaction among the configurations depicted in Fig. 1. The wave function for each configuration can be written as an



ground configuration LE configuration CT configuration

Fig. 1 ground and excited configurations for compounds (I) and (II)

antisymmetrized product of occupied MO's. For example, these functions are represented as follows:

$$\Psi_i^{CT} = \Phi_{rad}\,\chi \quad \text{(for CT configuration)} \quad \text{---------- (1)}$$

$$\Psi_j^{LE} = \Phi_{ion} \quad \text{(for LE configuration)} \quad \text{---------- (2)}$$

Here χ is 3d-orbital which is approximated by Slater's orbital taking an effective nuclear charge, Z_{3d}, as a parameter. Φ_{ion} and Φ_{rad} are the wave functions for cyclopentadienyl

anion and radical, respectively, which were cited from the literature.[5] Thus, four functions (ψ_1^{LE}, ψ_2^{LE}, ψ_3^{LE} and ψ_4^{LE}) are obtained for the LE configurations and twenty-six functions (ψ_1^{CT}, ψ_2^{CT}---- ψ_{26}^{CT}) for the CT configurations, besides Ψ_G for the ground configuration. The treatment of configuration interaction was carried out among these thirty-one functions. Taking the energy of the ground configuration as a standard, the energy values for the CT excited configuration were determined by eq. 3. The energies for the CT configuration were evaluated from the valence state ionization potential of 3d orbital (I_{3d}),[6] the electron affinity of cyclopentadienyl radical (A)[7,8] and Coulomb interaction energies. The resonance integrals between 2p- and 3d- orbitals were estimated from Mulliken's approximation.[9] Solving the secular equation constructed for (I) and (II), new energy levels (E_i) and wave functions (Ψ_i') are obtained. The lower five energy levels and their wave functions are as follows:

$$
\begin{aligned}
E_1 &= -1.038\ (eV) & \Psi_1' &= 0.937\Psi_G + 0.293\Psi_1^{CT} + 0.099\Psi_2^{CT} - 0.165\Psi_3^{CT} \\
E_2 &= 3.469 & \Psi_2' &= 0.000\Psi_G + 1.000\Psi_1^{CT} \\
E_3 &= 3.549 & \Psi_3' &= 0.096\Psi_G + 0.064\Psi_1^{CT} + 0.408\Psi_2^{CT} + 0.904\Psi_3^{CT} \\
E_4 &= 3.663 & \Psi_4' &= 0.000\Psi_G + 0.998\Psi_1^{CT} + 0.033\Psi_3^{LE} - 0.056\Psi_4^{LE} \\
E_5 &= 3.742 & \Psi_5' &= -0.135\Psi_G - 0.094\Psi_1^{CT} + 0.907\Psi_2^{CT} - 0.387\Psi_3^{CT}
\end{aligned}
\qquad (3)
$$

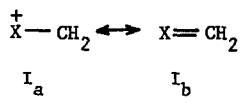
It is obvious that the ground state function corresponds to ylide structure judging from the coefficients of the component functions. For example, the contribution of ylide (Ψ_G) to the ground state wave function (Ψ_1') amounts to 88%. On the other hand, Ψ_2', Ψ_3', Ψ_4' and Ψ_5' correspond to ylene structure. Therefore, the transitions from Ψ_1' to Ψ_2', Ψ_3', Ψ_4' and Ψ_5' are interpretted as an intramolecular CT band corresponding to A band. This interpretation is comfirmed by the good agreement of calculated CT transition energy and oscillator strength with observed ones as shown in Table 2.

The ground state is lowered by 1.038 eV (24 Kcal) as compared with the unperturbed configuration. This stabilization energy is regarded as the resonance energy of I and II due to the resonance between ylide and ylene structures at the ground state. In conclusion, the ground state of cyclopentadienylides (I, II) has 88% of ylide and 12% of ylene structures. This means that ground state structure of cyclopentadienylides is substantially represented by the ylide structure, suggesting that the five membered ring has an aromatic character. This aromatic character was confirmed by π bond order-J_{vic} relationship and HMO calculation.[10] A possibility that the 6π electron delocalization in the cyclopentadienide ring governs the

Table 2 Calculated and Observed Transition Energy (TE) and Oscillator Strength (f) for the Intramolecular CT Band

Compound	Calculated Values		Observed Values (A band)	
	TE (eV)	f	TE (eV)	f
I	4.6	0.28	4.64	0.23
II	4.1	0.28	4.21	0.28

ylide structure of the cyclopentadienylide in the ground state is excluded, because the same treatment on the most simple ylide (I) without aromatic stabilization has also showed that I has 84% of ylide and 16% of ylene structures in the ground state.



I_a I_b

The result obtained predicts that for phosphonium and sulfonium cyclopentadienylides the electrophilic reactions easily take place but the Diels-Alder reactions are too difficult to occur.

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