CHEMISTRY LETTERS, pp. 1121-1124, 1972. Published by the Chemical Society of Japan

SPIN STATES OF METHYLENES PRODUCED FROM LEAST-MOTION DISSOCIATION OF ETHYLENE

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Spin states of methylenes produced from least-motion dissociation of ethylene were clarified by a semi-empirical CI method. Three lower-lying ^1A_g states of D_{2h} methylene-dimer at $R_{cc} = \infty$ were expressed in terms of the valence orbitals of two methylenes, and the states of two methylenes correlating to these states were determined.

In chemical reactions involving methylene, methylene is usually produced from the decomposition of molecules such as CH_2=CO and CH_2=N_2, and its spin state affects the successive reaction pattern. This note intends to show the results on the spin states of two methylenes produced from the least-motion dissociation of ethylene which were obtained using a semi-empirical SCF CI method including doubly excited configurations. The CI treatment, even if it is a limited one, is quite effective in correcting errors which are caused by the single-configuration calculation for a "forbidden" reaction process.[1,2]

All valence electrons of D_{2h} methylene-dimer were taken into account. Calculations were carried out for large C-C distances (R_{cc}>3.0A) with fixed CH_2 units in an idealized geometry: CH bond 1.10A, HCH angle 120°. The electron configuration of ethylene at large C-C distance is $(1a_g)^2(1b_{1u})^2(1b_{2u})^2(1b_{3g})^2(2a_g)^2(2b_{1u})^2$, with the lower-lying virtual orbitals following in the order $(1b_{3u})^0(1b_{2g})^0$.... Symbols σ, σ^*, π, and π^* were used for $2a_g$, $2b_{1u}$, $1b_{3u}$, and $1b_{2g}$ orbitals, respectively. In CI calculations, these four orbitals were selected for variable occupation.[3] SCF MO's and CI coefficients were determined using the INDO approximation.[4] Wave functions of three lower-lying ^1A_g states , the lowest of which may correlate to the ground state of normal ethylene, are listed in Table 1.

The electronic states of dissociated molecules are sometimes not easy to understand through the wave functions obtained by an ordinary Hartree-Fock method followed by a CI calculation. The state II in Table 1 represents the interaction of two singlet methylenes at $R_{cc}=\infty$. For the states I and III, however, an immediate answer can not be obtained from the wave functions in Table 1. This problem can be solved by expressing the wave functions in terms of MO's of two separate methylenes and by treating two methylenes independently. It is seen from Table 1[5] that the wave functions of the states I and III at $R_{cc} = \infty$ are given by:

$$\Phi_1 = \frac{\sqrt{3}}{4}(\Psi_1-\Psi_2-\Psi_3+\Psi_4) - \frac{1}{2}\Psi_6$$

$$\Phi_3 = \frac{1}{4}(\Psi_1-\Psi_2-\Psi_3+\Psi_4) + \frac{\sqrt{3}}{2}\Psi_6$$

Because of the simplicity of discussion, four electrons and four MO's, σ, σ^*, π, and π^*, are selected. Φ_1 and Φ_3 are expressed in terms of four valence orbitals of two methylenes, σ_1, p_1, σ_2, and p_2, using the relations: $\sigma=(\sigma_1+\sigma_2)/\sqrt{2}$, $\sigma^*=(\sigma_1-\sigma_2)/\sqrt{2}$, $\pi=(p_1+p_2)/\sqrt{2}$, and $\pi^*=(p_1-p_2)/\sqrt{2}$. Since two electrons in one methylene are independent of those in the other methylene at $R_{cc}=\infty$, it is possible that two electrons, 1 and 2, are assigned to one methylene and other two electrons, 3 and 4, to the other methylene. Electrons belonging to one methylene give no density on the other methylene at $R_{cc}=\infty$. Φ_1 and Φ_3 are expressed in terms of wave functions of two separate methylenes.[6)]

$$\Phi_1 = \frac{1}{\sqrt{3}}\{{}^3\phi_2{}^3\psi_2 - {}^3\phi_1{}^3\psi_3 - {}^3\phi_3{}^3\psi_1\}$$

$$\Phi_3 = {}^1\phi{}^1\psi$$

Table 1. Three lower-lying ${}^1A_g$ wave functions of ethylene for large C-C distances.

R_{cc}(A)		3.2			5.0		
State		I	II	III	I	II	III
Energy(eV)		-428.747	-427.714	-425.050	-428.526	-427.683	-424.947
Coefficients of	Ψ_0 *1	0.0111	0.9510	-0.0097	0.0000	0.9551	0.0000
	Ψ_1	0.3798	-0.0971	0.1856	0.4319	-0.1044	0.2492
	Ψ_2	-0.3709	-0.0826	-0.1835	-0.4317	-0.1044	-0.2490
	Ψ_3	-0.5136	-0.1229	-0.2872	-0.4343	-0.1051	-0.2509
	Ψ_4	0.4863	-0.1325	0.2601	0.4341	-0.1051	0.2508
	Ψ_5	-0.0078	-0.2158	-0.0113	0.0000	-0.2095	0.0000
	Ψ_6	-0.4666	0.0100	0.8840	-0.5000	0.0000	0.8660

*1 Configuration functions are:

$$\Psi_0 = |\ldots\sigma\bar{\sigma}\sigma^*\bar{\sigma}^*|,\quad \Psi_1 = |\ldots\pi\bar{\pi}\sigma^*\bar{\sigma}^*|,\quad \Psi_2 = |\ldots\pi^*\bar{\pi}^*\sigma^*\bar{\sigma}^*|,\quad \Psi_3 = |\ldots\sigma\bar{\sigma}\pi\bar{\pi}|,$$

$$\Psi_4 = |\ldots\sigma\bar{\sigma}\pi^*\bar{\pi}^*|,\quad \Psi_5 = \frac{1}{2}\{|\ldots\sigma\bar{\pi}\pi^*\bar{\sigma}^*|+|\ldots\pi\bar{\sigma}\sigma^*\bar{\pi}^*|+|\ldots\bar{\sigma}\bar{\pi}\sigma^*\pi^*|+|\ldots\sigma\pi\bar{\sigma}^*\bar{\pi}^*|\},$$

$$\Psi_6 = \frac{\sqrt{3}}{6}\{2|\ldots\sigma\bar{\pi}\sigma^*\bar{\pi}^*|+|\ldots\sigma\bar{\pi}\pi^*\bar{\sigma}^*|+|\ldots\pi\bar{\sigma}\sigma^*\bar{\pi}^*|+2|\ldots\pi\bar{\sigma}\pi^*\bar{\sigma}^*|-|\ldots\bar{\sigma}\bar{\pi}\sigma^*\pi^*|-|\ldots\sigma\pi\bar{\sigma}^*\bar{\pi}^*|\},$$

and singly excited configurations are not important for these three levels.

where,

$$^1\phi = \frac{1}{\sqrt{2}}\{|\sigma_1(1)\bar{p}_1(2)|+|p_1(1)\bar{\sigma}_1(2)|\}$$

$$^3\phi_1 = |\sigma_1(1)p_1(2)|$$

$$^3\phi_2 = \frac{1}{\sqrt{2}}\{|\sigma_1(1)\bar{p}_1(2)|-|p_1(1)\bar{\sigma}_1(2)|\}$$

$$^3\phi_3 = |\bar{\sigma}_1(1)\bar{p}_1(2)|$$

$$^1\psi = \frac{1}{\sqrt{2}}\{|\sigma_2(3)\bar{p}_2(4)|+|p_2(3)\bar{\sigma}_2(4)|\}$$

$$^3\psi_1 = |\sigma_2(3)p_2(4)|$$

$$^3\psi_2 = \frac{1}{\sqrt{2}}\{|\sigma_2(3)\bar{p}_2(4)|-|p_2(3)\bar{\sigma}_2(4)|\}$$

$$^3\psi_3 = |\bar{\sigma}_2(3)\bar{p}_2(4)|$$

Φ_1 and Φ_3 are now eigenfunctions of $S_1{}^2$ and $S_2{}^2$(subscripts indicate two CH_2) and from their eigenvalues it is found that Φ_1 and Φ_3 represent two triplet methylenes and two singlet (excited) methylenes, respectively. Φ_1 and Φ_3 are also eigenfunctions of $S^2(S=S_1+S_2)$, but don't have the antisymmetric property with respect to the exchange of two electrons belonging to different methylenes. This is permissible at $R_{CC}=\infty$ where two methylenes behave independently. After all, three lower-lying ^1A_g states of methylene-dimer dissociate into the following states of two methylenes at $R_{CC}=\infty$.

$$\mathrm{I} \rightarrow {}^3CH_2(^3B_1) + {}^3CH_2(^3B_1)$$

$$\mathrm{II} \rightarrow {}^1CH_2(^1A_1) + {}^1CH_2(^1A_1)$$

$$\mathrm{III} \rightarrow {}^1CH_2(^1B_1) + {}^1CH_2(^1B_1)$$

It is established here that the ground state of ethylene dissociates into two triplet methylenes. This is what has been pointed out by Basch.[2)] Basch calculated the dimerization of methylene using a non-empirical multi-configuration SCF method and found that the energy of the wave function $\Phi'=\frac{1}{2}(\Psi_1-\Psi_2-\Psi_3+\Psi_4)$ was lower than that of Ψ_0. As shown in the present note, the lowest state Φ' obtained by Basch does not correctly represent two triplet methylenes but the mixture of both two triplet and two singlet methylenes.

It is emphasized that a semi-empirical CI treatment gives reasonable results for a dissociation process and the electronic states of decomposition products can be verified by expressing the wave functions in terms of MO's of the products. The procedure mentioned above can be applied to all states of ethylene or other molecules. Especially, the results for $CH_2=CO$ and $CH_2=N_2$ are interesting, since they are actually used as the generator of methylene in chemical reactions. Discaussions on these problems and some comments on various semi-empirical CI calculations of the present reaction will be reported elsewhere.

References and footnotes.

1) K. Hsu, R.J. Buenker, and S.D. Peyerimhoff, J. Amer. Chem. Soc., 93, 2118 (1971); J.S. Wright and L. Salem, ibid, 94, 322(1972); W.H. Fink, ibid, 94, 1078(1972).
2) H. Basch, J. Chem. Phys., 55, 1700(1971).
3) Results presented here were not influenced by larger CI calculations in which 40 ^1A_g functions were included.
4) J.A. Pople, D. Beveridge, and P. Dobosh, J. Chem. Phys., 47, 2026(1967).
5) The analytic forms of Φ_1 and Φ_3 can also be obtained using the relations, $J_{\sigma\sigma}=J_{\sigma^*\sigma^*}=J_{\sigma\sigma^*}$, $J_{\pi\pi}=J_{\pi^*\pi^*}=J_{\pi\pi^*}$, and $K_{\sigma\pi}=K_{\sigma\pi^*}=K_{\sigma^*\pi}=K_{\sigma^*\pi^*}=(\sigma\pi|\sigma^*\pi^*)=(\sigma\pi^*|\sigma^*\pi)$, at $R_{cc}=\infty$. They are independent of the approximation method in evaluating the CI matrix elements.
6) If MO's of two methylenes, instead of MO's of methylene-dimer, are used as the basis orbitals in the CI calculation, the wave functions of States I and III at $R_{cc}=\infty$ are much easily obtained in terms of ϕ and ψ.

(Received August 28, 1972)