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INDO Molecular Orbital Interpretation of Thermal Singlet Oxygen-complex Generation by Strained Acetylenes

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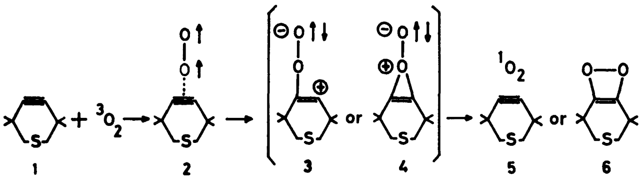
(Received February 16, 1979)

Synopsis. A three-center interaction between the $(\pi_u)_y$ of strained XC≡CX (X=H,F, or OCH_3) and the $(\pi_g)_y$ of $^3O_2$ separated the two half-occupied π_g MOs of $^3O_2$ on an energy scale of 428—494 kJ/mol causing spin inversion in $^3O_2$. A perepoxide-type $^1O_2$–XC≡CX intermediate once formed is transformed into a stable dioxetene-type $^1O_2$ complex from which the free generation of $^1O_2$ was found to be difficult.

The generation of $^1O_2$ has hitherto been realized by the reaction of sodium hypochlorite and hydrogen peroxide,[1–3] the decomposition of peroxides[4–8] and ozonides,[9–12] and the photosensitization[1,13,14] or microwave discharge[15,16] of $^3O_2$. The possibility of thermal $^1O_2$ formation from $^3O_2$ with 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne **1** has recently been reported:[17]



The above reaction mechanism, however, remains obscure. Consequently an INDO-MO[18] study of the above reaction process has been conducted using a simple model of the strained acetylene **1**, XC≡CX (X=H, F, or CH_3O), in order to shorten the computation time.

Results and Discussion

The strained acetylene molecule **1** is characterized by split π MOs, and the spectrophotometrically estimated energy difference between the π MOs is 30.5 kJ/mol at the strained angle (146°) of the acetylene **1** molecule.[17,19] In the case of XC≡CX, the energy difference between the π MOs has been estimated to be 170 kJ/mol (X=H), 89.5 kJ/mol (X=F), and 612 kJ/mol (X=CH_3O) at ∠XCC=146° using standard geometric parameters.[18] The destabilization of the $(\pi_u)_y$ MO expanding on the XC≡CX molecular plane ($(\pi_u)_y$ MO is energetically kept practically constant) is monotonically promoted by widening the strained angle thereby permitting overlap between the s or p AO of X and the p_y AO of C (overlap intergral=0.27 at 146° in HC≡CH). Therefore, the deviation of the C–X bond from the linear arrangement in XC≡CX makes the ionization energy of the highest doubly-occupied $(\pi_u)_y$ MO smaller and facilitates electron transfer from the strained acetylene molecule to $^3O_2$.

In view of the most reactive MOs of the strained acetylene and $^3O_2$, *i.e.*, the $(\pi_u)_y$ MO of the former and the π_g MOs of the latter, two distinctive interacting systems (three-center and four-center) may be considered as the mode of interaction between them (Fig. 1). The formation of a dioxetene-type intermediate from the strained acetylene and $^3O_2$ *via* the four-center interacting systems is however thermally forbidden since orbital symmetry in the σ-type orbital correlation such as $(\pi_g)_y-(\pi_g)_y$ or $(\pi_u)_y-(\pi_u)_y$ in the F-type interacting system should be inversely rearranged in the reaction process.[20] Therefore, the present thermal generation of $^1O_2$ from $^3O_2$ with the strained acetylene molecule must first pass through the three-center interacting system in which electron transfer from the $(\pi_u)_y$ MO in the acetylene to the $(\pi_g)_y$ (or $(\pi_g)_z$ in the B or C system) of $^3O_2$ would be expected together with back electron donation from the $(\pi_g)_x$ (and/or $(\pi_u)_x$) of the latter to the $(\pi_g)_y$ (or $(\pi_g)_z$ in the E system) of the former.

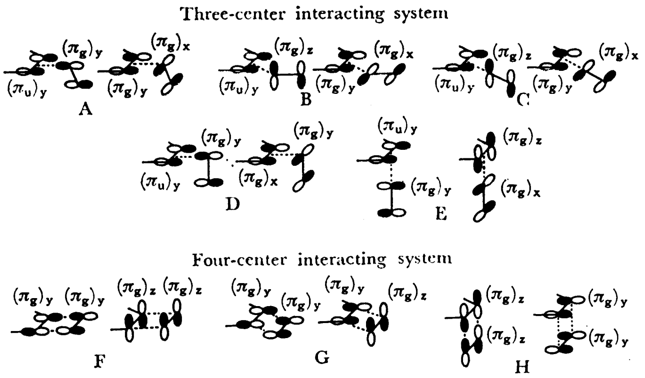
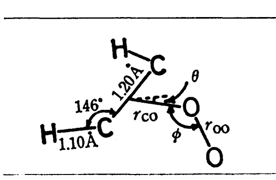


Fig. 1. Three-center and four-center interacting systems of the strained acetylene and $^3O_2$.

The three-center interacting systems of HC≡CH-$^3O_2$ were calculated utilising the geometric parameters in Table 1 and the relative stabilities of the interacting systems are given in the order: A>B>C>D>E. The one-electron attraction term (E_I) was large and negative in the order of D>A>E>B>C. The interelectronic and internuclear repulsions (E_{II} and E_N respectively) were larger and in the same order. The balance between the nuclear-electron attraction and the above repulsions results in the A-type interacting system being the most plausible mode of interaction.

The approach of the $^3O_2$ molecule to the strained acetylene in the A-type interacting system is an energy stabilization process and results in a quasi-stable perepoxide-type intermediate **2'**. For example, the potential curve for the HC≡CH-$^3O_2$ interacting system shown in Fig. 2, was obtained by optimizing the geometric parameters (see Table 1) by minimizing the total energies of the interacting systems with a repeated SCF-procedure.[21] As Fig. 2 illustrates, the change of electronic configuration from the triplet-state to the singlet-state interacting system could be expected

Table 1. Relative stabilities of the three-center interacting systems



	r_{CO}/Å[a)]	r_{OO}/Å	θ/deg.	φ/deg.	E_I/a.u.	E_{II}/a.u.	E_N/a.u.	E_{total}/a.u.
A	2.00	1.15	0	120	−188.7708	84.2764	54.5565	−49.9379
B	2.00	1.15	30[a)]	210[a)]	−186.9356	83.3466	53.6561	−49.9329
C	2.00	1.14	30[a)]	180[a)]	−186.6873	83.1985	53.5591	−49.9297
D	2.00	1.15	0	90[a)]	−192.5395	86.1563	56.4551	−49.9281
E	2.00	1.14	90	180[a)]	−187.7066	83.7018	54.0780	−49.9268

a) Fixed values in the calculations.

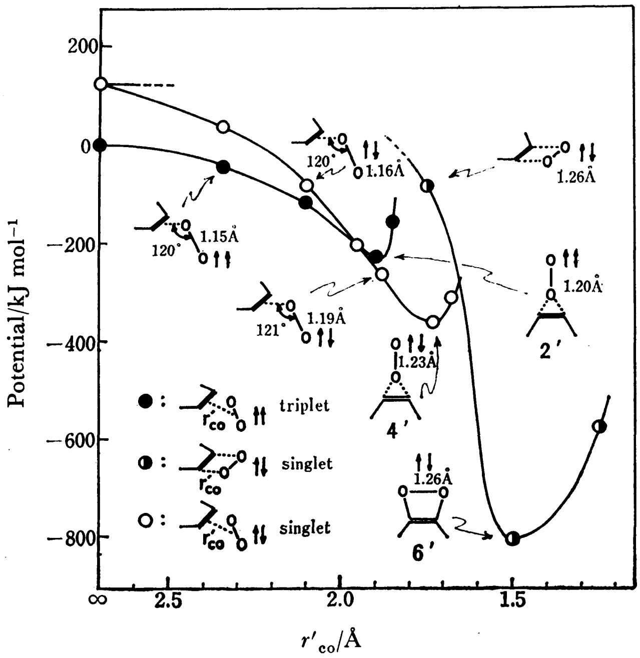


Fig. 2. Potential curves for the interacting system of the strained HC≡CH (∠HCC=146°) and $^3O_2$ or $^1O_2$. (The four-center interacting system of HC≡CH–$^1O_2$ at $r'_{CO}=\infty-1.8$ Å was not treated for shortening computation time.)

before the formation of the above-mentioned triplet-state intermediate **2′**. As the distance (r'_{CO}) between the two centers of C–C in HC≡CH and O–O in O_2 becomes smaller, the highest half-occupied MO formed by $(\pi_u)_y$ (HC≡CH)-$(\pi_g)_y(^3O_2)$ is destabilized with respect to the half-occupied MO of $(\pi_g)_y$(HC≡CH)-$(\pi_g)_x(^3O_2)$. The energy separation between the above two MOs are 194, 303, and 428 kJ/mol at $r'_{CO}=2.3$, 2.1, and 1.9 Å respectively. Such a remarkable energy separation between the two half-occupied MOs may result in an electronic rearrangement (*viz.*, electron migration from the $(\pi_g)_y$ MO to the $(\pi_g)_x$ MO in $^3O_2$ via spin inversion) by changing the triplet-state interacting system into the energetically more stable singlet-state system at the intersystem crossing point ($r'_{CO}=1.94$ Å). In the A-type interacting system of $CH_3OC≡COCH_3$ (or FC≡C)-$^3O_2$ (∠OCC=∠FCC=146°), the electron-donative (or attractive) nature of CH_3O (or F) resulted in the intersystem crossing at a slightly longer range of $r'_{CO}=1.96$ Å (or at a slightly shorter range of $r'_{CO}=1.91$ Å) with an energy separation between the above-mentioned half-occupied MOs of 485 kJ/mol (or 494 kJ/mol). The strained acetylene-$^1O_2$ system once formed *via* spin inversion, then, moves to a quasi-stable perepoxide-type intermediate **4′** (see Fig. 2). The singlet oxygen complex of the intermediate **4′**, then, transforms into a stable dioxetene **6′** (456 kJ/mol lower in potential energy than **4′**) with an activation energy of 58 kJ/mol. The generation of free $^1O_2$ from the dioxetene-type intermediate **6′** however appears difficult because the isolation of free $^1O_2$ from **6′** requires 920 kJ/mol (Fig. 2). Therefore, the reaction between $^3O_2$ and strained acetylenes such as **1** generates a dioxetene-type $^1O_2$ complex which thermally transforms into a dione with chemiluminescence (fluorescence).[17)]

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21) For instance, see K. Ohkubo, T. Yoshida, and K. Tomiyoshi, *Bull. Chem. Soc. Jpn.*, **49**, 2397 (1976).