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ON THE CONCERTED MECHANISM OF THE ENE REACTION OF SINGLET MOLECULAR OXYGEN WITH OLEFINS. AN AB-INITIO MO STUDY

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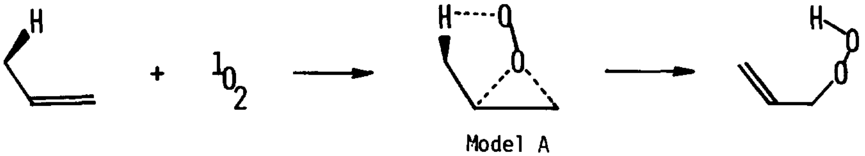
Summary: Ab-initio MO (4-31G) calculations were performed for the reaction of propene with singlet molecular oxygen. The theoretical result indicates that the concerted mechanism involves a model A-type transition state.

The mechanism of the ene reaction of singlet molecular oxygen with olefins has long been the subject of controversy.[1] Some years ago one of the authors showed by model calculations an important role of allylic hydrogen for the stabilization of the transition state (TST) of ene reactions of singlet oxygen ($^1O_2$).[2] The theoretical result based on a Murrell-type perturbation method predicted that the reaction path leading to the model A, where $^1O_2$ simultaneously attacks the allylic hydrogen and the center of the C-C double bond, is the most preferred in the case of propene-$^1O_2$ system, because of maximal CT interaction.[2a] A similar $^1O_2$-olefin aggregate (model A) has recently been proposed by Bartlett *et al.*,[3] Stephenson,[4] and Gollnick[5] as the TST of ene reactions in order to rationalize experimental results[1] including stereospecificity, deuterium isotope effects, solvent effects, and the so-called "cis" effect.[4,6]



Model A

In the present study we have performed ab-initio (4-31G) SCF calculations for the propene-$^1O_2$ system in order to evaluate the proposed mechanism. Fig. 1 illustrates the three reaction paths I, II and III examined in this study. Path I represents a reaction path involving a six-membered cyclic TST where $^1O_2$ synchronously attacks the allylic hydrogen and the terminal C-atom, whereas path II corresponds to the previous model A-type reaction path. Path III represents a $[_{\pi}2_s + _{\pi}2_a]$-type approach. Singlet unrestricted Hartree-Fock (^{1}UHF) and singlet projected UHF (^{1}PUHF) solutions have been used to calculate the energies of the aggregate between propene (1) and $^1O_2$, since the open-shell character of $^1O_2$ is still important at a relatively large intermolecular distance ($R > 2.3$ Å).[7] The potential curves obtained for these paths are depicted in Fig. 1. The relative energies of I-III at R = 2.5 Å are summarized in Table 1.

As is apparent from Fig. 1, the energies increase in the following order throughout the intermolecular distance examined;

path (II) < path (I) < path (III)

The concerted path II (model A) is the most preferred one in agreement with the previous perturbation calculations.[2a] The energy difference between I and II is quite large (4 kcal/mole) at R = 2.5 Å : this tendency is not altered even if the more extensive basis set (6-31G**) is utilized. Both reaction paths I and II are far more favorable than the $[_{\pi}2_s + _{\pi}2_a]$- like path III (Table 1). The present result, therefore, provides an important prediction that the hydroperoxide formation predominates over the dioxetane formation in the singlet oxygen reaction of simple olefins in a gas phase when they have axial allylic hydrogens.[1]

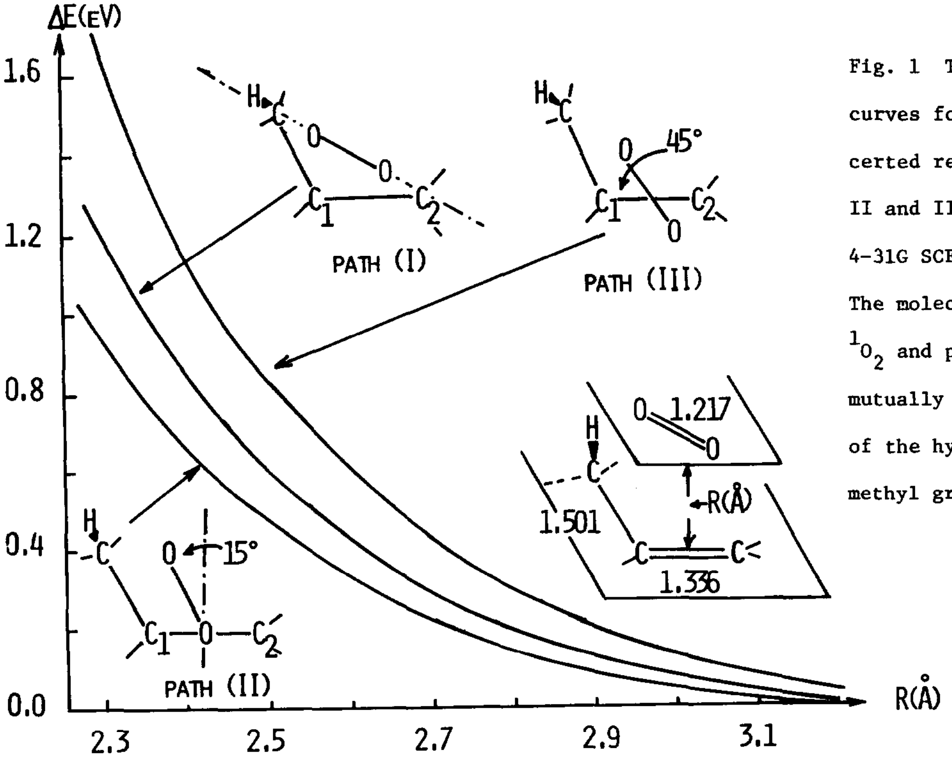
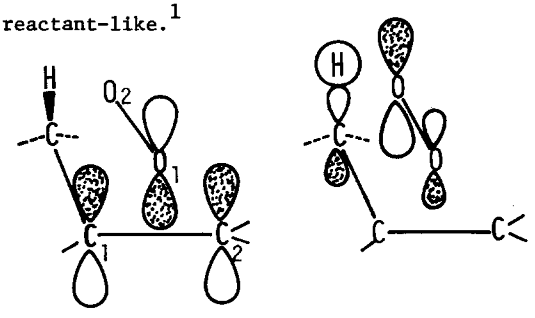


Fig. 1 The potential curves for the three concerted reaction paths I, II and III calculated by 4-31G SCF (^{1}UHF) method. The molecular planes for $^1O_2$ and propene are mutually parallel. One of the hydrogens of the methyl group is axial.

The 4-31G molecular orbitals respondible for the ene reaction are illustrated in Fig. 2. The HOMO of the aggregate (model A) essentially represents the $\pi(\underline{1}) - \pi^*(^1O_2)$ type interaction (B), not the interaction between the terminal O-atom ($^1O_2$) and allylic hydrogen. The latter interaction involved in a lower energy orbital is illustrated in C of Fig. 2. This implies that the C_2-O_1 and O_2-H (allylic) bond formation do not take place to the same extent in the transition state;the interaction between O_1-atom and π-bond of $\underline{1}$ is probably stronger than that between the O_2-atom and the allylic hydrogen in early stages of the reaction, *i.e.*, the two-stage model is suggested by these calculations.[8] If so, the primary deuterium isotope effect[4] for ene reaction may be small ($k_H/k_D < 2$) and the C-H bond elongation might not be conspicuous in the TST region, not incompatible with the experimental result that the TST for ene reaction is reactant-like.[1]



B C

Fig. 2 The HOMO (B) and lower MO (C) for propene plus $^1O_2$ system by 4-31G method.

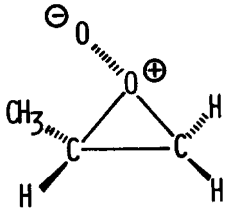
Table 1 Relative stabilities (kcal/mole) among the reaction paths I, II and III by ab-initio SCF calculations (R = 2.5 Å)

Path	Singlet		Triplet
	^{1}UHF	^{1}PUHF	^{3}UHF
I	2.87	4.12	1.71
II	0.0[a)]	0.0[b)]	0.0[c)]
III	8.78	12.64	6.93

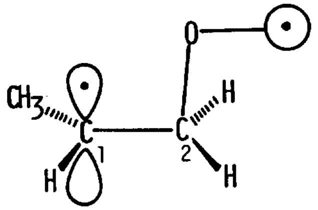
a) -266.249, b) -266.222, c) -266.273 (h).

The potential curves obtained for the concerted paths I-III by the SCF 4-31G method are repulsive in nature as shown in Fig. 1. Nevertheless, the present result cannot rule out the possibility of the formation of a "contact" exciplex in the sence of Lewis and Ware[9] before reaching the TST, *i.e.*, the possibility of the two-stage concerted mechanism passing through an oriented π-complex.[8] It is interesting to note that a model A-type TST is proposed to be involved in the "so-called" two-stage concerted mechanism of the Diels-Alder reaction by Woodward and Katz.[10] In order to evaluate this possibility more extensive CI calculations combined with geometry optimizations are certainly necessary.

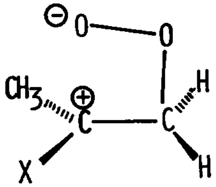
Two-step mechanisms involving perepoxide[11] and 1,4-biradical[12] have been repeatedly proposed for ene reactions of simple olefins. However, perepoxide intermediate (D) is less stable than 1,4-biradical in both ab-initio VB[12] and MO[13] calculations. Furthermore, the rotational barriers around the C_2-C_1 bond of 1,4-biradical (E) is too small to rationalize the stereospecificity observed in ene reactions.[13] The concerted mechanism passing through a "bonded" TST like model A (path II) is far more compatible with the available experimental data as pointed out by Stephenson.[14]



D



E



F (X = OR, NR_2)

The two-step mechanism involving a 1,4-zwitterion (ZW) has been proposed for ene reactions of enol ethers[14] and enamines.[15] As reported previously,[15c] ene reactions of enol ethers should proceed through a concerted mechanism at least in non-polar solvents, whereas the ZW mechanism (F) is certainly plausible in the case of enamines. Thus the mechanism of ene reactions seem to be dependent on the electron-donating ability of substituents and on the solvent polarity. The exact determination of the TST for ene reactions of simple olefins is in progress.[16]

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