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ON THE MECHANISM OF ENE REACTION OF ELECTRON-RICH OLEFINS WITH SINGLET OXYGEN. AB-INITIO MO CALCULATIONS

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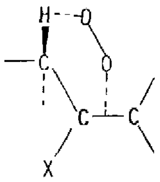
Summary: The ab-initio MO (STO-3G) calculations were performed for the reaction of 2-aminopropene with singlet oxygen.

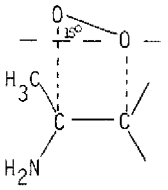
There is much current controversy on the mechanism of the ene reaction of olefins with singlet oxygen ($^1O_2$).[1] The mechanisms proposed are the (i) one[1a]- and two[2]-stage concerted, (ii) stepwise involving a diradical,[3] (iii) stepwise involving a perepoxide,[4] and (iv) stepwise involving a zwitterionic intermediate.[5] In a previous paper[2a] we have demonstrated by Murrel-type perturbation calculations[6] the importance of a simultaneous attack of $^1O_2$ on allylic hydrogen and the center of the C-C double bond (model A) in the ene reaction of $^1O_2$ with propene. Since the diradical character of $^1O_2$ disappeared in the hydrogen-transfer stage of the model A owing to the allowed orbital interactions,[7] the two-stage concerted mechanism passing through a oriented π-complex (model A) was proposed for the ene reaction of non-polar olefins.[2] However, for electron-rich olefins such as enol ethers or enamines the attack of $^1O_2$ on the terminal carbon is expected to become more important in the ene reaction as well as in the $[_{\pi}2 + {}_{\pi}2]$ cycloaddition. In fact, perturbation calculations indicated that the model B is the lowest in interaction energy among several other models, including perepoxide intermediates, in the case of 2-aminopropene-$^1O_2$ system.[2a] We also demonstrated by INDO-RHF CI method that the reaction of enamines such as 1,2,3-trimethylindole proceeds via a zwitterionic intermediate, not by way of perepoxide or 1,4-diradical.[5b] In order to confirm these conclusions reliable *ab-initio* MO calculations are necessary.

Model A



X = H, OR

Model B



We have examined the *ab-initio* MO (STO-3G) calculations[8] for 2-aminopropene-$^1O_2$ system. The unrestricted Hartree-Fock (UHF) and singlet projected UHF (^{1}PUHF)[9] methods were used instead of the restricted HF (RHF) method, since the σπ-diradical character[9a] of $^1O_2$ did not disappear in the relatively large intermolecular distance ($R > 2.1$ Å) (Table 1). The four different reaction paths leading to zwitterion- (B, B') and perepoxide-type intermediates (P, P') were examined, and the potential energy curves for each path are illustrated in Fig. 1. As apparent from Fig. 1, the total energies for the reaction paths increase in the following order;

B (β-attack) < B' (α-attack) < P (NH_2-side attack) < P' (CH_3-side attack)

The β-carbon attack (B) of $^1O_2$ is much favorable than the α-carbon attack (B') throughout the intermolecular distance R examined (Fig. 1). This may also be understandable from the HOMO-LUMO interaction (Fig. 2).[4a] Thus, the theoretical treatment clearly shows the high regioselectivity in the interaction of 2-aminopropene with $^1O_2$. Both perepoxide models P and P' are unfavorable in energies as compared with the $[_\pi 2 + _\pi 2]$ type approach B, in agreement with the perturbation calculations.[2a]

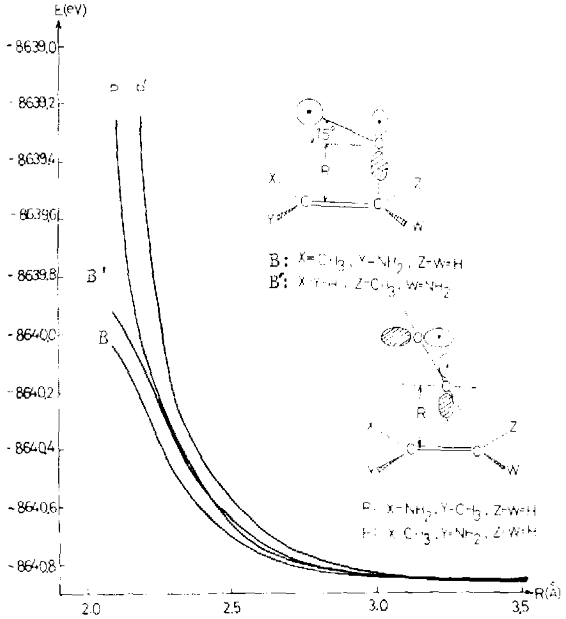
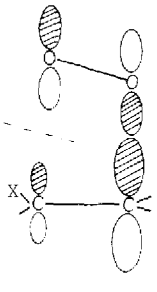


Fig. 1

Table I. Relative Stabilities (kcal/mol) among the Intermediates (B, B', P, P') by *ab-initio* STO-3G Calculations (R = 2.3 Å)

Type	Singlet UHF	Singlet ^{1}PUHF	Triplet UHF
B	0.0[a]	0.0[b]	0.0[c]
B'	2.7	3.7	1.6
P	3.3	5.3	1.4
P'	5.9	7.4	4.3

[a] -317.548. [b] -317.531. [c] -317.674 (h).



X = electron donor

Fig. 2

While σπ-diradical (DR) state is the ground singlet state in the reaction path B in the relatively large R-region, the zwitterionic (ZW) state becomes most stable in the samll R-region, owing to 1,4-Coulombic interaction as indicated previously.[2,5b] Then the avoided surface crossing takes place as illustrated in Fig. 3. From the result of Fig. 3, following three reaction modes are expected to occur; (I) allylic hydrogen abstraction by the peroxide anion portion of the ZW intermediate, (II) allylic hydrogen abstraction by the terminal O-radical of the DR (σπ) intermediate, and (III) ring closure of ZW to form 1,2-dioxetane. It should be noted here that the allylic hydrogen is a little far away from the p-type orbital of the terminal O-atom in the cisoid conformation as shown in Fig. 3. Thus rotation around the C_1-C_2 axis is necessary for the allylic hydrogen abstraction.[5a,c] Since the C_1-C_2 bond is essentially a single bond for both DR (σπ) and ZW intermediates, the internal rotation may be facile. Therefore it seems reasonable to assume that the lifetimes of ZW and DR are closely related to the occurrence of the reactions I,II and III. The lifetime of ZW will be long enough to undergo ene reaction at least in polar solvents.[5a,10]

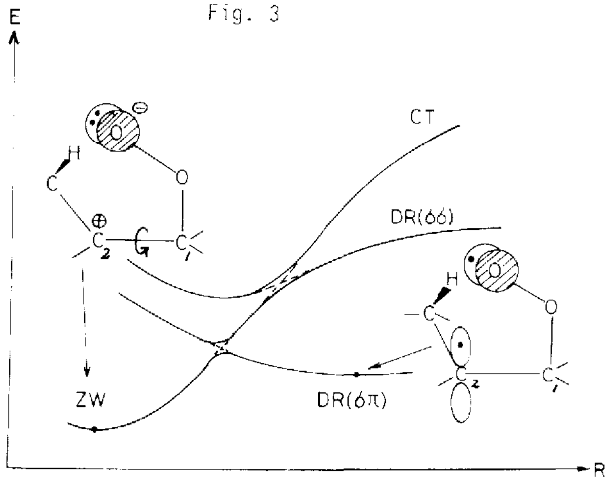
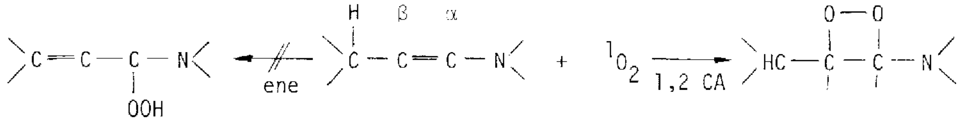
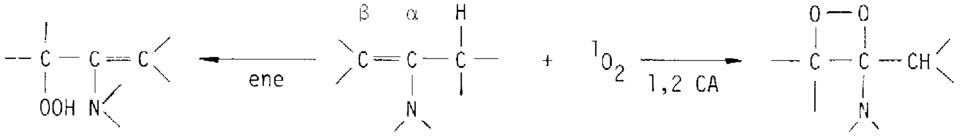


Fig. 3

Experimentally, enamines are known to undergo $[_{\pi}2 + {}_{\pi}2]$ cyclo-addition with $^1O_2$ to form dioxetanes.[11] No ene reaction has been observed with enamines having allylic hydrogens attached to β-carbons (Eq. 1).[11] In contrast, we have recently observed that certain enamines having allylic hydrogens at α-carbon site can undergo ene reaction in competition with the dioxetane formation in aprotic solvents (Eq. 2).[5a] The observed regiospecificity is in good agreement with the theoretical predictions described above.



(Eq. 1)

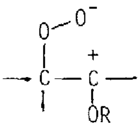


(Eq. 2)

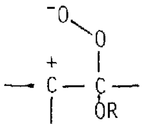
We also observed that protic solvents retard the ene reaction of Eq. 2 and enhance the 1,2-cycloaddition reaction.[5a] This might also be explained by decrease of the ability of hydrogen abstraction of peroxy anion of ZW by H-bonding with alcohol. Thus, the experimental results are reasonably explained in terms of a ZW mechanism which may also be supported by the present calculations. In fact, ZW intermediates are interceptable by alcohols in certain cases.[5a] Perepoxide- and two-stage concerted mechanisms are unfavorable in the enamine-$^1O_2$ reaction.

In the case of enol ethers allylic hydrogen at the β-carbon site is abstractable by $^1O_2$, in sharp contrast to the case of enamines.[12] As can be recognized from the HOMO-LUMO interaction[4a] in Fig. 2, the α-attack should be less favorable than β-attack. Thus, it seems unlikely that ZW is involved in the singlet oxygenation of enol ethers at least in non-polar solvents.[13] In this case the interaction of type A (model A) might become important since electron donating ability of alkoxy group is much weaker than that of amino group. Then one- or two-stage concerted mechanism such as model A seems to be a reasonable alternative for the ene reaction of enol ethers in non-polar solvents, in accordance with recent Stephenson's proposal.[14] However, in polar protic solvents the ZW mechanism will become equally important as in the case of enamines.[15] It should be emphasized that ZW of type C is much favorable than that of type D, in contrast to ealier proposals.[5c, 12]

Type C



Type D



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