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Ab Initio Molecular Orbital Studies of Singlet Oxygen Reactions of Olefins, Enol Ethers, and Enamines

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Ab initio molecular orbital (MO) studies of singlet oxygen reactions of olefins, enol ethers, and enamines were carried out. The relative stabilities of biradical (BR), the so-called perepoxide-like (PE), perepoxide-like zwitterionic (PEZW) and zwitterionic (ZW) intermediates for singlet oxygen reactions of these species are described theoretically, together with their ionization potentials, molecular structures and solvation energies. The activation energies for the ene and dioxetane formation reactions were found to be determined by the electron-donating properties of substituents introduced to these substrates. The following conclusions were drawn from these calculated results: (1) A nonradical transition state with a PE-like conformation is the most plausible for ene reactions of allylic olefins and enol ether with allylic hydrogens. (2) A BR mechanism is favorable for the (2+2) reactions of singlet oxygen with simple olefins in the gas phase. (3) A nonconcerted mechanism via polar (PEZW, ZW) intermediates is operative for (2+2) cycloadditions of unsymmetrical enol ethers in the solution phase, whereas the (2a+2a) mechanism and a two-step mechanism via the PE intermediate are conceivable for the (2+2) reactions of symmetrical olefins in the solution phase. The implications of these theoretical results to the mechanisms of singlet oxygen reactions are discussed in relation to various experimental results, such as the stereochemistry, isotope effects, solvent effects and laser-photolysis experiments.

The accumulation of (i) theoretical evidence[1—3] on undetectable short-lived intermediates[4—8] and transition states clustered by solvents, (ii) information about very short-lived intermediates experimentally available by laser techniques,[9] and (iii) stereochemical evidence and isotope experiments[10] have allowed us to propose the most plausible reaction mechanisms of singlet oxygen reactions.[11] In previous papers,[3,12] we emphasized, on theoretical grounds, the importance of classifying olefins into symmetrical (groups **III**, **IVs**) and unsymmetrical (groups **I**, **II**, **IVu**) groups in order to understand systematically their reaction modes toward singlet oxygen ($^1O_2$). In fact, previous calculations have shown that the reaction mechanisms of $^1O_2$ are highly dependent of the electron-richness and symmetry of olefins, which are classified into **I**—**IVs**. For example, the model B transition structure (TS) is favored over the model A TS for the ene reactions of both symmetrical and unsymmetrical allylic olefins. The former corresponds to oxiranium-1-oxide (the so-called perepoxide (PE))-like TS in an organic chemist's sense, while the latter is the classical six-membered TS by Gollnick.[7] PM3 calculations[13] were carried out to locate both model A and B TSs (Chart 1), which showed that the activation barriers for A and B TS are 28.3 and 30.2 kcal mol^{-1}, respectively; the former is slightly more favorable (only 1.9 kcal mol^{-1}) than the latter in the gas phase; this tendency is reversed in a polar solution because of the stronger solvation of model B TS or PE-like TS.[12] On the other hand, (2s+2s) cycloadditions (model G) via zwitterions (ZW)[3,12,14] have been shown to be the most favorable for unsymmetrical electron-rich olefins (Chart 2).[3a] However, the concerted (2s+2a) cycloaddition (model M) seems to be reasonable for symmetrical olefins **III** and **IVs**.[3a,12]

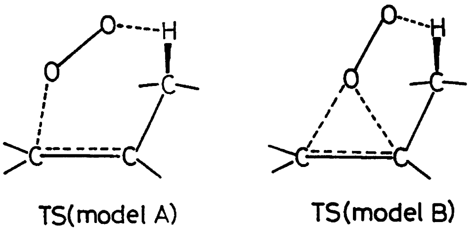

Chart 1.

Experimentally, the product distributions, solvent effects on the reaction modes and other mechanistic characteristics are variable, depending on the types of olefins, as typically seen in the singlet oxygen reactions of enol ethers (Chart 3).[10] In accord with these experimental trends, the preceding ab-initio calculations[3] concerning the reaction intermediates have clearly indicated that the relative stabilities

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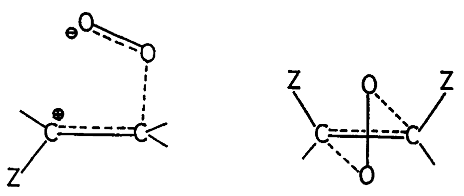

TS(model G) TS(model M)

Chart 2.

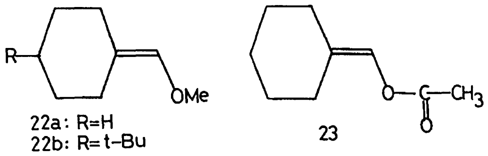

22a: R=H
22b: R=t-Bu
23

Chart 3.

among biradical (BR), PE and ZW intermediates and TS are highly dependent on the molecular structures of the substrates and solvation energies.

During the past decade, there have been theoretical arguments[1–3,13] concerning the mechanism of the ene reaction of olefins and enol ethers possessing allylic hydrogens.[6,7,11] Both concerted and two-step mechanisms involving the BR, PE, or ZW intermediate were proposed.[13–33] In previous papers[3] we pointed out that a two-step mechanism involving BR is inconsistent with the available experimental data for the ene reactions of these olefins, and proposed on theoretical grounds a nonradical mechanism via the model B TS or the PE-like TS for the ene reactions of allylic olefins in the solution phase,[21] although a purely theoretical location[12] of the TS in solution phase is difficult to attain, even at the present stage. The intermolecular configuration interaction (CI) predicted the formation of a π-complex as a precursor of the model B TS. Later, laser techniques clearly demonstrated the formation of π-complexes between singlet oxygen and several types of olefins, such as enol ethers.[9]

In addition to the classical cis effect for the ene reactions of trisubstituted olefins,[23–25] the gemi-directing effect and nonbonding large group interactions[30–33] have attracted much current interest in connection with the mechanism of single oxygen ene reactions. Clennan et al.[31] have reported steric and electronic effects on the regiochemistry for the ene reactions of 22 allylically substituted tetramethylethylenes. Their molecular-mechanics calculations have revealed that the site of hydrogen abstraction is correctly predicted by the rotational barriers of the methyl groups. This is in accord with previous ab initio results.[26] Recently, Adam and Nestler[33] have conducted singlet oxygen reactions of chiral allylic alcohols, showing hydroxy-directed regio- and diastereoselectivity. Thus, the applications of singlet oxygen ene reactions to chiral synthesis have received current interest.

As a continuation of previous work,[3,12,21,26] in this paper, the most plausible mechanisms of ${}^1O_2$ reactions are discussed based on computational results, and as well as a consideration of laser experiments,[9] and other results, such as molecular-beam experiments in the gas phase,[15,17] isotope effects[10] and trappings with aldehydes and alcohol,[5] and the stereochemistry of ene reactions.[27–33]

Relative Stabilities of Intermediates for Singlet Oxygen Reactions

1. Relative Stabilities of Intermediates for Unsymmetrical Olefins. Since many experimental results[13–29] have been explained by assuming perepoxide (PE) and/or zwitterion (ZW) intermediates in singlet oxygen reactions, we now examine their electronic structures in both gas and solution phases. As previously shown,[3] the PE, ZW and perepoxide-like zwitterion (PEZW) intermediates have polar or ionic structures which are well described by the closed-shell restricted Hartree–Fock (RHF) solution. Therefore, full geometry optimizations of three intermediates were carried out using the energy gradient technique based on the RHF/4-31G solution. The net charges on the terminal carbon and oxygen atoms, calculated for ZW by the RHF approach, are largely positive and negative, respectively, in accord with the zwitterionic character.[3] Similarly, the ZW character is remarkable, even in the case of the PE-like conformation of an ionic intermediate formed between an unsymmetrical electron-rich olefin and singlet oxygen. Therefore, this is referred to as PEZW (Chart 4).

The RHF solution of the BR intermediate indicates a triplet instability, being reorganized into the more stable singlet unrestricted Hartree–Fock (UHF) solution. In fact, the singlet UHF solution provides the σ- and π-radical orbitals which are responsible for BR($\sigma\pi$). The geometry of BR($\sigma\pi$) was fully optimized by the energy gradient technique of the singlet UHF/4-31G solution. Since the singlet UHF solution involves triplet spin contamination, an approximate but size-consistent spin projection (AP) was carried out in order to improve the total energy. The total energy by APUHF was close to those of the complete active space (CAS) config-

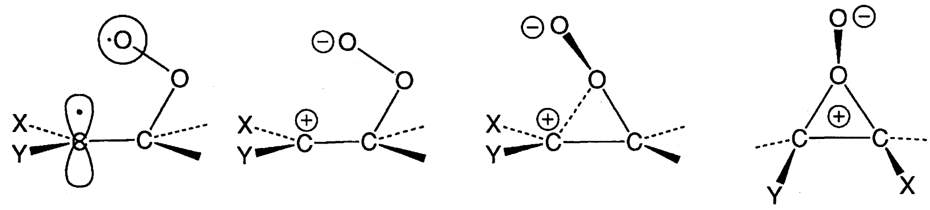

BR($\sigma\pi$) ZW PEZW PE

Chart 4.

uration interaction (CI) by using the singlet UHF natural orbitals (UNO) and UNO CASSCF. The details concerning the APUHF, UNO CASCI, and UNO CASSCF have been given elsewhere.[3e)]

Here, the energy difference between BR and the closed-shell ion X ($\Delta E_{\text{X-BR}}$) was calculated using the total energies of the corresponding APUHF and RHF/4-31G energies,

$$\Delta E_{\text{X-BR}} = E(\text{RHF}) - E(\text{APUHF}), \tag{1}$$

where X=ZW, PEZW and PE. The BR-ZW gaps calculated by Eq. 1 are summarized in Tables 1 and 2.

Since ZW or PEZW is formed by an intramolecular charge-transfer from the terminal carbene group (CXY) to the terminal oxygen, the BR-ZW energy gap should be given by[3f)]

$$\Delta E_{\text{ZW-BR}} = I_{\text{p}}(\text{CXY}) - E_{\text{A}}(\text{O}) - J, \tag{2}$$

where $I_{\text{p}}(\text{CXY})$ and $E_{\text{A}}(\text{O})$ are the ionization potential and electron affinity, respectively, and J is the electron-hole attraction energy. As shown in a preceding paper,[3)] the relative stabilities among the BR, PE, and ZW intermediates for singlet oxygen reactions of unsymmetrical olefins are indeed highly dependent on the electron-donating properties of the introduced substituents. The previous results are consistent with the relationship given by Eq. 2. It therefore seems to be reasonable that the observed ionization potentials (I_{p}) of these olefins correlate to the properties.[12)] The calculated BR-ZW gaps ($\Delta E_{\text{ZW-BR}}$) in Table 1 are plotted against the observed I_{p} (eV) of the unsymmetrical olefins ($XYC=CH_2$), i.e., **1** (X=Y=H), **2** (X=Me,Y=H), **3** (X=Y=Me), **4** (X=OMe,Y=H), and **9** (X=Me,Y=OMe). As expected, the correlation is good, as shown in Fig. 1, and the following relation is obtained:

$$\Delta E_{\text{ZW-BR}} = 14.8 I_{\text{p}} - 81.8 \quad (\text{kcal mol}^{-1}). \tag{3}$$

Equation 3 was then applied to estimate the energy gaps for other enol ethers and for enamines. The results are given in Tables 1 and 2, respectively.

Similarly, the calculated energy gaps between BR and perepoxide-like zwitterion (PEZW) are also plotted against the observed I_{p} of **2**—**4** and **9**, as shown in Fig. 1. The correlation line is given by

$$\Delta E_{\text{PEZW-BR}} = 5.97 I_{\text{p}} - 14.3 \quad (\text{kcal mol}^{-1}). \tag{4}$$

Equation 4 was also applied to estimate the PEZW-BR gaps for other enol ethers and enamines. The results are summarized in Tables 1 and 2.

The moderate (II) and strong (III) solvation energies, ΔE_{S} for PEZW, were assumed to be 27 and 39 kcal mol^{-1}, respectively, whereas they were taken to be 39 and 51 kcal mol^{-1} for ZW, respectively, on the basis of ab-initio MO calculations of clusters consisting of peroxy intermediates and waters.[3)] The energy gaps for BR, PEZW, and ZW, modified by the solutions, are given in Tables 1 and 2.

From Table 1, the BR intermediate is more stable than the polar (ZW,PEZW) intermediates for simple alkenes (**1**—**3**), even in the strong solvation model (model III). PEZW is more stable than ZW as the polar intermediates, showing the order of stabilization of the intermediate given by case A in Table 3. This result implies that the (2+2) reactions passing

Table 1. Relative Stabilities among the BR, PEZW, and ZW Intermediates for Alkenes and Enol Ethers Plus Singlet Oxygen Systems

No.	Substrates	I_{p}	$\Delta E_{\text{ZW-BR}}$[a,c)]			$\Delta E_{\text{PEZW-BR}}$[b,c)]		
		eV	I	II	III	I	II	III
1	$CH_2=CH_2$	10.51	74(73)	35	23			
2	$MeCH=CH_2$	9.73	62(63)	23	11	44(44)	17	5
3	$Me_2C=CH_2$	9.23	55(52)	16	4	41(40)	14	2
4	$MeOCH=CH_2$	9.14	53(57)	14	2	40(41)	13	1
5	$EtOCH=CH_2$	9.07	52	13	1	40	13	1
6	*i*-PrOCH=CH$_2$	8.89	50	11	−1	39	12	0
7	*n*-BuOCH=CH$_2$	8.87	49	10	−2	39	12	0
8	*t*-BuOCH=CH$_2$	8.75	48	9	−3	38	11	−1
9	Me(MeO)C=CH$_2$	8.58	45(44)	6	−6	37(37)	10	−2
10t	(*E*)-MeOCH=CHEt	8.65	46	7	−5	37	10	−2
10c	(*Z*)-MeOCH=CHEt	8.57	45	6	−6	37	10	−2
11t	(*E*)-*t*-BuOCH=CHMe	8.68	47	8	−4	38	11	−1
12t	(*E*)-EtOCH=CHMe	8.55	45	6	−6	37	10	−2
12c	(*Z*)-EtOCH=CHMe	8.53	44	5	−7	37	10	−2
13t	(*E*)-(MeO)CH=CMe(*c*-Pr)[d)]	8.2	39	0	−12	35	8	−4
14	Me(MeO)=CHMe	8.20	39	0	−12	35	8	−4
15	(MeO)$_2$C=CHMe$_2$	8.0	37	−2	−14	34	7	−5
16	MeOCH=CPh$_2$	7.76	33	−7	−19	32	5	−7
17	(*E*)-MeOCH=CMe(*c*-Pr)	8.0	37	−2	−14	34	7	−5
18	Dihydropyran	8.35	42	3	−9	36	9	−3

a) I(gas phase), II($\Delta E_{\text{s}} = 39$), and III($\Delta E_{\text{s}} = 51$), b) I(gas phase), II($\Delta E_{\text{S}} = 27$), and III($\Delta E_{\text{S}} = 39$) (kcal mol^{-1}), c) Values by the ab-initio MO calculations are given in parentheses, d) *c*-Pr means cyclo-Pr.

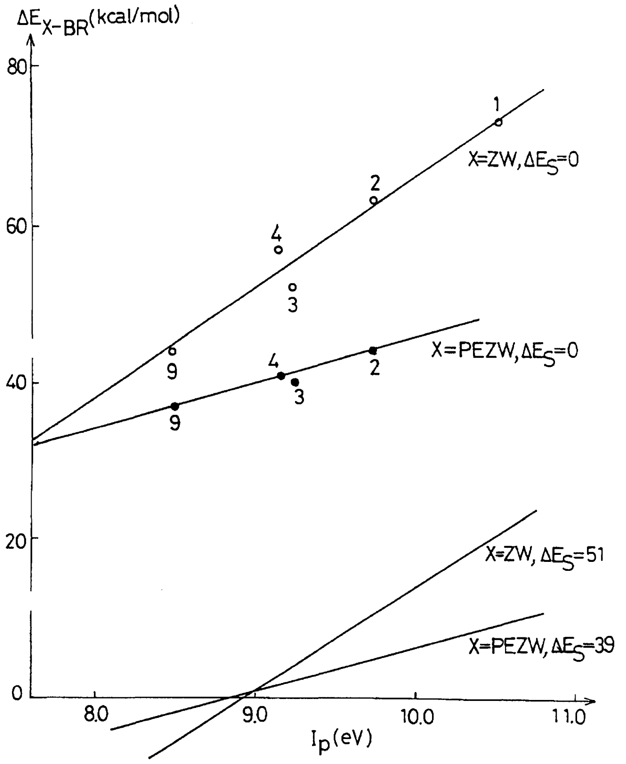


Fig. 1. A plot of the variation in the energy difference ΔE_{X-BR} between X (ZW or PEZW) and BR against the ionization potentials of substrates in Table 1. ΔE_S is the strong solvation energy for ZW or PEZW.

through polar intermediates, such as PE or ZW, are hardly acceptable for allylic olefins (**1**—**3**). On the other hand, dioxetane formations via the BR intermediates need activation energies of over 10 kcal mol^{-1}[17] even in the solution phase, since polar solvents cannot drastically stabilize the BR transition state, as confirmed by ab-initio calculations.[3] Therefore, the ene reactions, which have activation energies lower than 5 kcal mol^{-1},[7,15] become the most probable in the singlet oxygenation of allylic olefins in both the gas and solution phases.

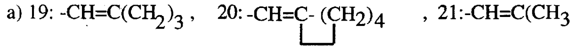
In the gas phase, BR is the most stable for all of the enol ethers examined here. However, PEZW is more stable than ZW, showing relation A in Table 3. BR is still the most stable for alkyl vinyl ethers (AVE) **4**—**8**, even in the intermediate solvation model (II); however, ZW and PEZW are nearly degenerate in energy, as shown by case B in Table 3, whereas for AVE **9**—**12** ZW becomes more stable than PEZW, as shown by case C. While ZW is the most stable for AVE **14**—**17**, even in intermediate solvation, as shown by the case D.

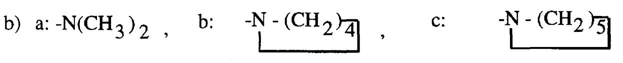
On the other hand, the BR, PEZW, and ZW intermediates are nearly equally stabilized for alkoxy vinyl ethers **4**—**8** in the case of strong solvation model(III) as shown by relation E. For AVE (**9**—**13**), ZW is slightly more stable than PEZW, whereas PEZW and BR are nearly equally stabilized, as shown by case F in Table 3. Though polar intermediates become more stable than BR for AVE (**14**—**17**), ZW is more favorable as an ionic intermediate than PEZW, as shown by relation G in Table 3.

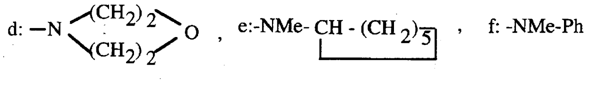
The perepoxide with 1,4-dipolar property (PEZW), instead of zwitterion (ZW), may play an important role as a polar

Table 2. Relative Stabilities among the BR, PEZW, and ZW Intermediates for Enamines

No.[a,b]	I_p	$\Delta E_{ZW\text{-}BR}$[c]			$\Delta E_{PEZW\text{-}BR}$[d]		
	eV	I	II	III	I	II	III
19a	7.46	29	−10	−22	30	3	−9
19b	7.10	23	−16	−28	28	1	−11
19c	7.4	28	−11	−23	30	3	−9
19d	7.6	31	−8	−20	31	4	−8
20a	7.56	30	−9	−21	31	4	−8
20b	7.14	24	−15	−27	28	1	−11
20c	7.50	29	−10	−22	31	4	−8
20d	7.67	32	−7	−29	32	5	−7
21b	7.79	33	−6	−18	32	5	−7
21c	7.95	36	−3	−15	33	6	−6
21d	8.20	39	0	−12	35	8	−4
21e	7.88	35	−4	−16	33	6	−6
21f	7.11	23	−16	−28	28	1	−11


a) 19: $-CH=C(CH_2)_3$, 20: $-CH=C-(CH_2)_4$, 21: $-CH=C(CH_3)_2$


b) a: $-N(CH_3)_2$, b: $-N-(CH_2)_4$, c: $-N-(CH_2)_5$


d: $-N(CH_2)_2O(CH_2)_2$, e: $-NMe-CH-(CH_2)_5$, f: $-NMe-Ph$

c) I(gas phase), II($\Delta E_S=39$), and III($\Delta E_S=51$), d) I(gas phase), II($\Delta E_S=27$), and III($\Delta E_S=39$) (kcal mol^{-1}).

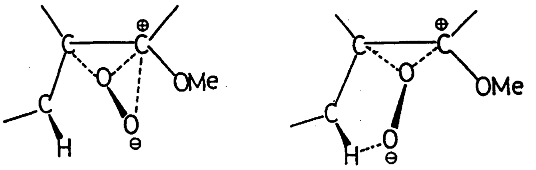
Table 3. Relations of Stabilities among BR, PEZW, and ZW Intermediates for Alkenes and Enol Ether, and Enamine Plus Singlet Oxygen Systems

Case	Relations	Solvation	Systems
A	BR>PE(PEZW)>ZW	I	Simple alkenes (**1**—**3**)
B	BR>PEZW≅ZW	II	Alkyl vinyl ethers (**4**—**8**)
C	BR>ZW>PEZW	II	Alkyl vinyl ethers (**9**—**12**)
D	ZW≅BR>PEZW	II	Vinyl ethers (**14**—**17**)
E	BR≅PEZW≅ZW	III	Alkyl vinyl ethers (**4**—**8**)
F	ZW>PEZW≅BR	III	Alkyl vinyl ethers (**9**—**13**)
G	ZW>PEZW>BR	III	Enamines disubstituted ethers (**14**—**17**)
H	ZW>BR>PEZW	II	Enamines
I	BR>PE>ZW	I	Symmetrical olefins
J	PE>BR>ZW	II.III	Symmetrical olefins

intermediate in cases A, B, and E, whereas ZW is the most plausible polar intermediate in the other cases: C, D, F, and G. Since BR is most stable in cases A and B, PEZW is particularly important for case E; namely, for less electron-rich enol ethers in a polar solution.

Relations A—C in Table 3 indicate that the (2+2) reactions of enol ethers via polar intermediates are hardly acceptable in the gas phase and a less polar solution. The same reactions via the BR transition state (TS)[3] need significant activation energies (over 10 kcal mol^{-1}), as shown below, being suppressed at low temperatures. The ene reactions are in turn the most favorable for enol ethers with allylic hydrogens in such a reaction condition. On the other hand, dioxetane formations via ZW are feasible even in a less polar solution for electron-rich enol ethers **14**—**17**, because of relation D. They become easier for species in polar solutions, as shown in F and G in Table 3. The (2+2) reactions via ZW are expected to be accelerated at low temperatures, since the orientations of polar solvents are accompanied by a large loss of the activation entropies (negative entropies).[12,14]

It seems appropriate to examine a few examples for explanations. Enol ether **22** is one of the AVE's like **14**—**17**. Therefore, the ene reaction[3,12] is the most favorable in the gas phase and in nonpolar solutions (e.g., benzene), whereas both ene and (2+2) cycloaddition via ZW become feasible in less polar solvents, such as CH$_2$Cl$_2$ and methyl acetate, in agreement with the experimental results obtained by Ashveld and Kellogs.[4] The trapping product derived from ZW of **22** was detected in a methanol solution.[4] On the other hand, according to Wilson and Schuster,[5b] only the ene product is available for enol acetate (**23**) in both acetone and methanol. The present theory favors the ene reaction[21] in these solutions, as in the case of 2-methyl-3-(substituted phenyl)-2-butene[6] and allylic olefins,[7] since the electron donating ability of the acetoxy group in **23** is as weak as that of the alkyl groups, compared with the methoxy group in **22**. It should be noted here that the optimized geometry[3d] of the PEZW for **22** has a conformation (**24**) that favors a (2+2) cycloaddition reaction rather than a conformation (**25**) for hydrogen abstraction (Chart 5), although Wilson and Schuster[5b] favor a two-step mechanism via perepoxide for an ene reaction of **23**. We will return to this subtle problem after a further examination of the mechanisms for the ene reactions.

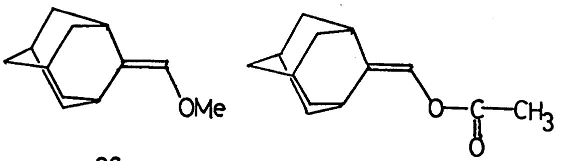


24:(2+2)　25: ene

Chart 5.

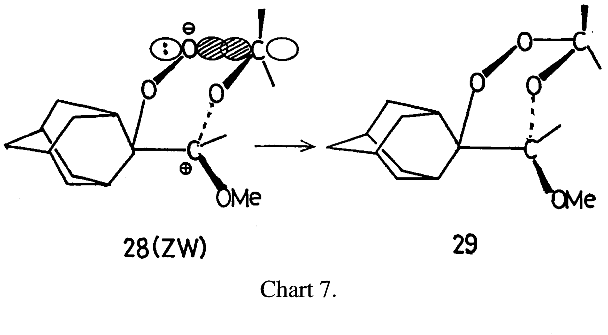
Other interesting examples are adamantylidene derivatives, **26** and **27** (Chart 6). The BR mechanism could be operative for dioxetane formation from **26** in the gas phase, since **26** is a substituted enol ether. In fact, **26** reacts even with triplet oxygen at 200 °C.[3c] On the other hand, the (2+2) cycloaddition of **26** can proceed via ZW in less polar and polar solutions because of relations D and G in Table 3. Jefford et al.[5a] have shown that a ZW intermediate can be trapped by acetaldehyde in its neat solution, providing a 1,2,4-trioxane (**29**) (Chart 7). Saito et al.[8a] have also shown that a trapping product by trimethylsilyl cyanide is detected in the case of the ^{1}O$_2$ reaction of **26** in CH$_2$Cl$_2$ and acetonitrile. Theoretical relationships D and G in Table 3 are compatible with these experiments.

On the other hand, **27** undergoes an acyl transfer to the terminal oxygen of PEZW (or ZW) in acetone, and a (2+2)



26　27

Chart 6.



28(ZW)　29

Chart 7.

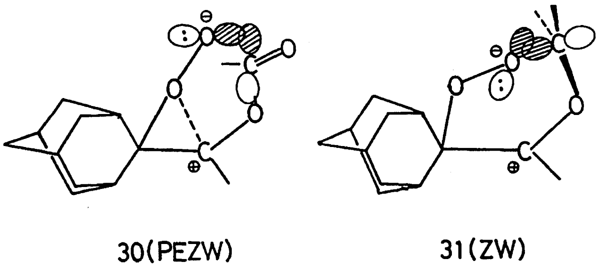
cycloaddition in methanol. Wilson and Schuster[5b)] have proposed the intermediacy of a perepoxide **30** for both the acyl and (2+2) cycloaddition of **27**. In the present classification, **27** may correspond to case E in Table 3, in conformity with their proposal. The proposal seems to be reasonable, since the acetoxy group is less electron-donating. However, the possibility of ZW (**31**), particularly for a (2+2) cycloaddition in methanol, cannot be ruled out, at least based on the present theoretical calculations (Chart 8).

The BR intermediates are more stable than the ZW intermediates for enamines in the gas phase (the relation C in Table 3). This trend is, however, opposite, even in the intermediate solvation model (II); however, PEZW is still less stable than BR, as shown by case H in Table 3. On the other hand, both the polar intermediates, ZW and PEZW, are more stable than BR in the strong solvation model, showing relation G in Table 3. Therefore, ZW play essential roles for the singlet oxygenation of enamines as well as indole derivatives, which were previously thoroughly investigated.[8)] It is noteworthy that ene reactions are suppressed for type-II enamines because the peroxide anion of the more stable ZW (**32**) cannot abstract an allylic hydrogen (Chart 9). Saito et al.[8)] have indicated experimental results which are consistent with the theoretical result.

2. Relative Stabilities of Intermediates for Symmetrical Olefins. The ab-initio MO calculations have shown that the BR-PE energy gaps for symmetrical olefins correlate with the electron-donating abilities of the introduced substituents. The energy gaps ($\Delta E_{\text{PE-BR}}$) calculated by Eq. 1 are plotted against the ionization potentials (I_p) of the symmetrical olefins (XYC=CXY): **34** (X=Me, Y=H), **36** (X=OMe, Y=H), **37** (X=OEt, Y=H), and **43** (X=Y=OMe). The correlation is good, providing the following relation:

$$\Delta E_{\text{PE-BR}} = 4.63 I_p - 20.0 \quad (\text{kcal mol}^{-1}). \tag{5}$$

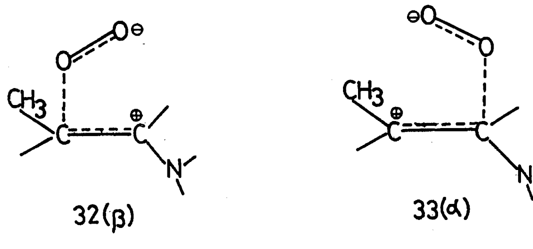
Equation 5 was then applied to calculate the BR–PE gaps



30(PEZW)

31(ZW)

Chart 8.



32(β)

33(α)

Chart 9.

for other symmetrical olefins. The results are given in Table 4. The BR-ZW energy gaps for symmetrical olefins were assumed to be equal to the corresponding gaps for unsymmetrical olefins (XYC=CH_2): **2**—**5** and **44** (X=Y=OMe).[3e)] The obtained BR-ZW gaps are plotted against the ionization potentials of **34**–**37** and **43**. The correlation line is given by

$$\Delta E_{\text{ZW-BR}} = 12.8 I_p - 53.6 \quad (\text{kcal mol}^{-1}). \tag{6}$$

The BR-ZW gaps of other symmetrical olefins were estimated by using Eq. 6. The results are given in Table 4.

The solvation energies for PE and ZW of symmetrical olefins were taken as being the same as those of PEZW and ZW for unsymmetrical olefins, respectively.[3e)] The energy gaps, modified by the solvations, are given in Table 4. From Table 4, although PE is more stable than ZW for symmetrical olefins, BR is more stable than these ionic intermediates in the gas phase (case I in Table 3). However, PE becomes more stable than BR in a polar solution; interestingly, ZW remains less stable than PEZW, even if the strong solvation model is employed. Therefore, the PE intermediate plays an important role for singlet oxygen reactions of symmetrical electron-rich olefins (**III**, **IVs**) in solution (case J in Table 3).

Activation Energies for Ene and (2+2) Reactions

There has been much theoretical controversy[1—3)] concerning whether ene and (2+2) cycloaddition proceed through a common intermediate (perepoxide or biradical). Here, theoretical estimations of the activation energies of these reactions are carried out on the basis of the preceding ab-initio MO results. Ab-initio MO calculations[3)] indicate that the Hammett's σ_I-value is a useful parameter for estimating the $\Delta E_{\text{ZW-BR}}$ values, because $^1O_2$ acts as an electron acceptor.[12)] Thus, the σ_I-value can be used to estimate activation parameters of the ene and (2+2) reactions, which pass through early transition states. Figure 2 shows variations in the observed gas-phase activation energies (E_a) for both the ene and (2+2) reactions plotted against the a σ_I-value of the substituents. The E_a-values for the ene reactions vary inversely with the σ_I-value, giving a straight line plot, whereas those of (2+2) reactions exhibit a different behavior, yielding a curved line. By using the correlation lines in Fig. 2, we can estimate the activation energies for the ene and (2+2) reactions of other olefins. The obtained results obtained are summarized in Table 5. Table 5 shows that there is a significant difference in the activation energies of the $^1O_2$ ene and (2+2) reactions in the case of alkenes and enol ethers. Hence, the transition states of these reactions modes must be different, at least in the gas phase. The possible reaction paths for the ene and (2+2) reactions in the gas phase are depicted in Fig. 3. Here, a model B TS with the PE-like orientation, instead of the traditional concerted path via model A TS is proposed for the ene reactions of olefins with allylic hydrogens on the basis of previous theoretical studies.[3,12,21)] Whereas a mechanism involving nonpolar BR TS or BR intermediates has been assumed for the (2+2) reactions of alkenes and enol ethers, since the polar intermediates, such as perepoxide and zwitter-

Table 4. Relative Stabilities among the BR, PE, and ZW Intermediates for Symmetrical Olefins Plus Singlet Oxygen Systems

No.	Substrates	I_p	$\Delta E_{\text{PEZW-BR}}$[a,c]			$\Delta E_{\text{ZW-BR}}$[b,c]		
		eV	I	II	III	I	II	III
34t	(*E*)-2-Butene	9.12	22(22)	−5	−17	63(62)	24	12
34c	(*Z*)-2-Butene	9.12	22(22)	−5	−17	63(62)	24	12
35	2,3-Dimethyl-2-butene	8.30	18(17)	−9	−21	52(55)	13	1
36t	(*E*)-1,2-Dimethoxyoethylene	8.38	19(19)	−8	−20	53(53)	14	2
36c	(*Z*)-1,2-Dimethoxyethylene	8.39	19(19)	−8	−20	54(53)	15	3
37t	(*E*)-1,2-Diethoxyethylene	8.23	18(19)	−9	−21	51(52)	12	0
37c	(*Z*)-1,2-Diethoxyethylene	8.15	18(19)	−9	−21	50(52)	11	−1
38a	2,3-Dihydro-1,4-dioxin	8.35	19	−8	−20	53	14	2
39	3,4-Diaryl-3-hexane	8.10	17	−10	−22	50	11	−1
40	Stilbestrol	8.1	17	−10	−22	50	11	−1
41	Adamantylidene-AD	8.10	17	−10	−22	50	11	−1
42	1,2-Diphenylcyclobutene	8.10	17	−10	−22	50	11	−1
38b	2,3-Dihydro-5,6-bis(*p*-hydroxyphenyl)-1,4-dioxin	7.24	14	−13	−25	39	0	−12
38c	2,3-Dihydro-5,6-bis(*p*-methoxyphenyl)-1,4-dioxin	7.29	14	−13	−25	39	0	−12
38d	2,3-Dihydro-5,6-bis(*p*-methylphenyl)-1,4-dioxin	7.40	14	−13	−25	41	2	−10
38e	2,3-Dihydro-5,6-diphenyl-1,4-dioxin	7.49	15	−12	−24	42	3	−9
38f	2,3-Dihydro-3,5,6-tetraphenyl-1,4-dioxin	7.45	14	−13	−25	42	3	−9
43	Tetramethoxyoethylene	7.5	15(14)	−12	−24	42(40)	3	−9

a) I(gas phase), II(ΔE_S=27), and III(ΔE_S=39), b) I(gas phase), II(ΔE_S=39), and III(ΔE_S=51) (kcal mol^{-1}), c) ab-initio values are in parentheses.

Table 5. Observed and Estimated Activation Energies of the Singlet Oxygen (2+2) an Ene Reactions in the Gas Phase (kcal mol^{-1})

Substrates	σ_t[a]	E_a(2+2)[b]	E_a(ene)[c]	np* Product[d]
Ethylene (**1**)	0.0	21.4		HCHO
(*E*)-2-Butene (**34t**)	0.34	(11—13)	7.3	CH_3CHO
2-Methyl-2-butene	0.51	(8—10)	4.9	CH_3CHO
2,3-Dimethyl-2-butene (**35**)	0.68	(6—8)	3.2	$(CH_3)_2CO$
Methyl vinyl ether (**4**)	0.27	13.5		HCHO
Ethyl vinyl ether (**5**)	0.27	12.5		HCHO
Butyl vinyl ether (**7**)		13.0		HCHO
2-Methoxypropene (**9**)	0.44	11.8	(6—8)	CH_3CHO
(*Z*)-1-Methoxypropene		(12—13)	(6—8)	CH_3CHO
(*E*)-1-Methoxypropene		(12—13)	(6—8)	CH_3CHO
1,1-Diethoxyethylene	0.54	(7—9)		HCHO
(*Z*)-2-Methoxy-2-butene (**14c**)	0.61	(6—8)	(3—5)	CH_3CHO
(*E*)-2-Methoxy-2-butene (**14t**)	0.61	(6—8)	(3—5)	CH_3CHO
1-Ethoxy-2-methylpropene	0.61	(6—8)	(3—5)	$(CH_3)_2CO$
2-Methoxy-3-methyl-2-butene	0.78	(5—7)	(1—3)	$(CH_3)_2CO$
1,1-Dimethoxy-2-methylpropene (**15**)	0.88	(4—6)	(0—1)	$(CH_3)_2CO$
1-Aminoethylene	0.66	(6—8)		HCHO[e]
1-Aminopropene	0.83	(4—6)		CH_3CHO[e]
N,*N*-Diethylaminoethylene	0.83		(4—6)	HCHO
1-(*N*,*N*-Dimethylamino)-2-methylpropene	1.17	2.16		—[f]
1,1-Diaminoethylene	1.32	(1—2)		HCHO
Tetrakis(dimethylamino)ethylene	3.32	(<0)		—[g]
2-Bromopropene		14.8		HCHO
1,1-Difluoroethylene		16.3		HCHO
Ketene		15.2		HCHO
Ketene-*d*		14.3		DCHO
Allene		18.6		HCHO
3-Methyl-1,2-butadiene		14.8		HCHO; $(CH_3)_2CO$

a) Sum of Hammett's σ_{para} values of substituents, b) observed values in Ref. 14 and calculated values from Fig. 2 in parentheses, c) observed values in Ref. 13 and calculated values from Fig. 2 in parentheses, d) observations in Ref. 13, e) estimated products from the Markovnikov rule for biradical (zwitterion) formations, f) polymerization, g) not observed, h) concerted (2a+2s) path instead of noncencerted paths may be operative.

ion are unstable in the gas phase, as shown in Tables 1 and

2, a mechanism via ZW is reasonable for very electron-rich

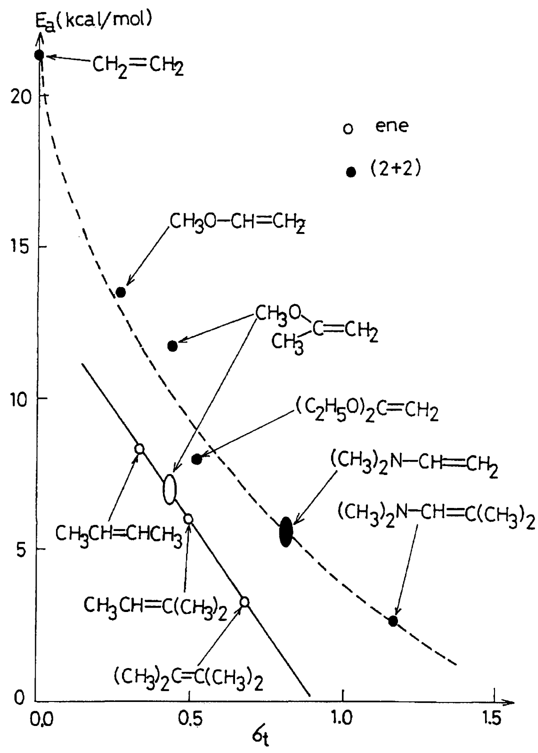


Fig. 2. A plot of the variation in the observed activation energies (E_a) for the (2+2) cycloaddition and ene reaction of $^1O_2$ with olefins against the sum of Hammett's σ_{para} values of the substituents.

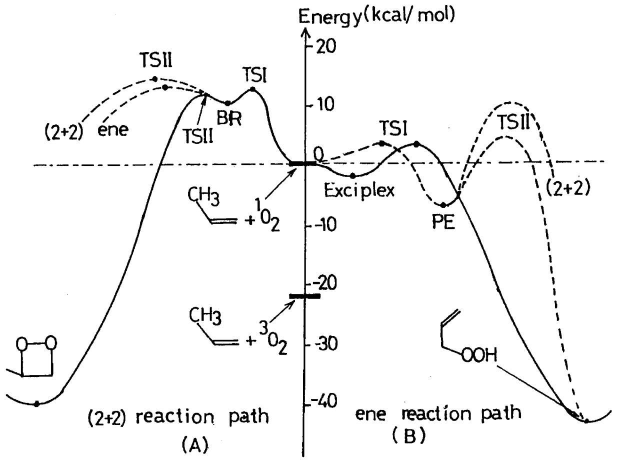


Fig. 3. Proposed potential curves for the (2+2) and ene reactions between $^1O_2$ and unsymmetrical olefins (or enol ethers). (A) TSI and TSII are early and late transition states for the (2+2) reactions between $^1O_2$ and olefins (or enol ethers). The dashed line shows the late TSII for ene and (2+2) reactions according to the Goddard mechanism which path through a common biradical (BR) intermediate. (B) The dashed line shows the late TSII for ene and (2+2) reactions according to the Dewar's mechanism which path through a common peroxide (PE) intermediate.

enamines, such as N,N-dimethyl-2-methyl-1-propenylamine (DPA).

From Tables 1, 2, 3, and 4, plausible potential curves for the (2+2) reactions can be constructed, as illustrated in **a**—**c** of Fig. 4. The activation energies (E_a) are over 5 kcal mol^{-1}, even for the electron-rich enol ethers.[17] Judging from this magnitude, an exciplex (or encounter complex) formation stage is not a TS for these species, at least in the gas phase. This implies that the E_a values are not determined by only the electron-donating ability (σ_t) of the enol ethers; other factors, such as the molecular deformation of the species, are not negligible, even at an early TS. The potential curve for this case is illustrated by type **a** in Fig. 4. On the other hand, the E_a values are only 2.6 kcal mol^{-1} for DPA,[13] and zero for diaminoethylene (DAE) in Table 5. Therefore, the potential curves for the (2+2) reactions of these species correspond to cases **b** and **c** in Fig. 4, respectively. Therefore, the exciplex formation stage becomes a rate-determining step for DPA and DAE, even in the gas phase, indicating that the observed E_a value should be parallel to the electron-donating (σ_t) abilities of the species. Obviously, the controlling factors of the E_a values in the case of the alkenes and enol ethers differ from those of the enamines, yielding a curved line, as depicted in Fig. 2.

The inclusion of the solvation energies changes the potential curves for the (2+2) reactions of enol ethers from those in the gas phase. Obviously, the polar intermediates (PEZW and ZW) exhibit paramount solvation effects, as shown in Tables 1 and 4. Thus, the potential curve of type **a** for these species in the gas phase may be converted to type **b** (or **c**) by solvation, as illustrated in Fig. 4. The conversion from type **a** to **b** (or **c**) implies a moderate acceleration of the (2+2) cycloaddition rate, since the relatively late TS for the type **a** curve has a moderate ionic character. On the other hand, such acceleration should be very small if substrates, such as DPA, have type-**c** potential curve, even in a nonpolar solution: very early TS has a negligible ionic character,[12] and hence the solvation effects to the TS are minor.

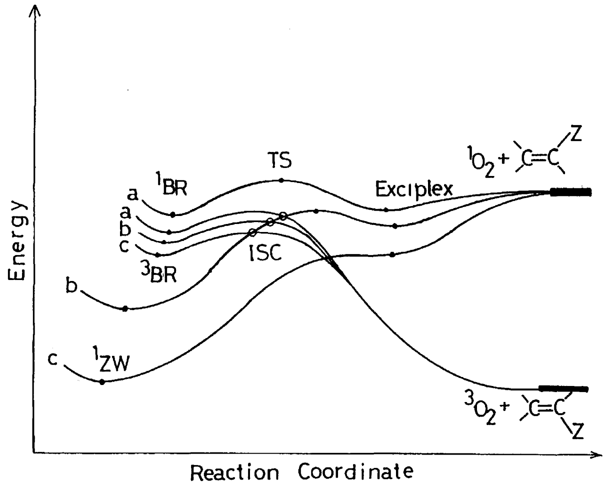


Fig. 4. Potential energy curves for (2s+2s)-like approaches between $^1O_2$ and donor olefins. TS indicates the transition state, and ISC denotes the points of intersystem crossing. a, b, and c are weak, intermediate and strong electron donors, respectively (see text).

Gorman et al.[9)] have observed a significant solvent effect upon the quenching of $^1O_2$ by 2-methoxynorbornene. The quenching rate in cyclohexane was too slow to determine the activation parameters by their technique, whereas it was accelerated by about 56 times in acetonitrile. This is compatible with the type-**a** curve in Fig. 4 for the (2+2) cycloaddition of the species in a nonpolar solution. The ZW-BR gaps in Table 1 suggest similar rate accelerations for other enol ethers. If the rate-determining step is cyclization from ZW (or PEZW) to dioxetane, the solvent effect for the reaction rate is probably over 1000,[14)] as recognized from the large solvation energies for ZW, as shown in the preceding paper.[3)] Although this is not the case for the $^1O_2$ reaction, it is the case of ZW (2+2) cycloadditions of tetracycanoethylene (TCNE) and enol ethers, as shown by Steiner and Huisgen.[14)]

The present mechanisms are considerably different from the others: (i) Dewar and Thiel[1)] have shown that a ZW-like TS is the rate-determining step for singlet oxygen reactions of enol ethers, and the (2+2) cycloaddition proceeds directly through ZW, while the ene reaction occurs after the formation of perepoxide, which comes from ZW, and (ii) Harding and Goddard[2)] have considered biradicals as common intermediates for both the ene and (2+2) reactions of enol ethers. Since the observed and calculated activation energies for the ene and (2+2) reactions are different, the mechanisms require that the transition state for the formation of a common intermediate (zwitterion or biradical) should not be a rate-determining step: namely, the TS would be late if these two step mechanisms are truly operative. This is, however, in contradiction with the molecular beam experiments by Cross, Jr. et al.[15)] and the observed solvent effects.[9)]

Mechanisms for Ene and (2+2) Reactions of Olefins and Enol Ethers

1. Gas Phase Reactions of Unsymmetrical Olefins. The intermolecular CI[12)] and ab-initio MO results[3)] on the BR, PE, and ZW intermediates are consistent with the model B TS with a PE-like conformation for the ene reactions of alkenes and enol ethers with allylic hydrogens in the gas phase. However, since several other mechanisms have been theoretically proposed,[1—3,18)] a careful examination of both the experimental and theoretical results seems to be necessary.

Ashford and Ogryzlo[16)] have determined the activation energies (E_a) for the ene reactions of olefins in the gas phase. They have shown that in the gas phase the large variation in the reactivity of allylic olefins can be attributed almost entirely to differences in the activation energy (E_a), since the preexponential factor changes very little between the reactants. The E_a-values are in the range from 3.2 to 7.5 kcal mol^{-1}, and are parallel to the ionization potentials (I_p) of the substrates, as shown in Table 6. The have arrived at a simple ene mechanism involving a concerted six-membered TS with a small charge-transfer (CT) character, since the activation barriers in the gas phase are reduced by about 3 kcal mol^{-1} in the solution phase. A previous perturbation calculation[12)] indeed showed about a 10% CT character, compatible with their experiments. They have denied the intermediacy of a bound intermediate, such as a perepoxide in the gas phase, in accord with the ab initio results given in Tables 1 and 2.

Cross, Jr., et al.[15)] carried out a crossed molecular-beam study on the singlet oxygen reactions of 1,1-diethoxyethylene, 2-methoxypropene and enamines, such as DPA. They have shown that dioxetane formation must occur in a single bimolecular collision, and is promoted by translational energy. This indicates that its transition state is early, and hence, reactant like. They could detect chemiluminescence only at 673 K in the case of the (2+2) type reaction between 2-methoxypropene and $^1O_2$. The activation energy which they observed for the (2+2) reaction is over 10 kcal mol^{-1}, whereas it is known to be only a few kcal/mol for the ene reaction (see Table 4). Accordingly, they concluded that the two reactions proceed by quite different paths and do not involve a common intermediate. Obviously, their conclusion is in contradiction with the two-step mechanisms of Dewar[1)] and Goddard.[2)] In contrast, it is quite consistent with the present reaction-path models in Fig. 3. Cross, Jr. et al.[15)] observed the radical polymerizations of *N*, *N*-dimethyvinylamine in their gas-phase oxygenations. This is compatible with the greater stability of BR than ZW, even for the species in the gas phase, as shown in Table 2.

Bogan et al.[17)] have also investigated the $^1O_2$ reactions of ketenes, enol ethers and enamines in a gas-phase flow system at high temperature (330—700 K). They observed chemiluminescence arising from the decomposition of dioxetanes formed by the $^1O_2$ reactions of these species. The quantum yields (ϕ) for singlet excited carbonyl products were also

Table 6. Activation Energy Barriers Estimated for Substituted (Z) Trimetylethylene

Substituents	σ_I	(2s+2s)		ene	
		Gas[a)]	Solution[b)]	Gas[a)]	Solution[b)]
H	0.51	8—10	9	4.9	2
$Si(CH_3)_3$	0.52	8—10	9	4—6	2
$C(CH_3)_3$	0.71	5—7	6	4—6	1
Br	0.28	11—13	12	8—10	6
Cl	0.24	12—14	13	9—11	7
$COOCH_3$	0.06	16—18	15	13—15	11
$COCH_3$	0.01	21—23	22	14—16	12

a) Estimated values from Fig. 2. b) Estimated values from gas-phase E_a-values.

measured. The ϕ-value for 2-methoxypropene was 1/7 of the corresponding value for ethyl vinyl ether, although they estimated that the relative ratio should be lower than 1/55 if the activation energy (E_a) for hydroperoxide formation (ene reaction) is lower by about 5 kcal mol^{-1} than the E_a-value for dioxetane reaction. They have explained this dioxetane-favoring tendency on the basis of Goddard's mechanism,[2] according to which the initial attack of $^1O_2$ upon an alkene leads to a •CCOO• biradical for both the ene and dioxetane formation reactions. For 2-methoxypropene, although two •CCOO• biradicals, **44** and **45**, could be formed, only **44c** can undergo the 1,5-hydrogen transfer necessary to form allylic hydroperoxide, as illustrated in Fig. 5. Since Goddard's mechanism predicts that path α is more favorable than path β, because of anomeric effects due to the alkoxy group, the ene reaction should be suppressed, as is indeed observed.[17] In order to test the above hypothesis, they further studied the $^1O_2$ reaction of 1-ethoxypropene. However, chemiluminescence of modest intensity was observed despite their expectation that the ene reaction would be enhanced. Namely dioxetane formation was not suppressed. Thus, the gas-phase data are not consistent with a two-step mechanism involving a BR as a common intermediate.[2]

Hammond[19] has reported that (*E*)-2-methoxy-2-butene reacts cleanly with $^1O_2$ in the gas phase to give tertiary hydroperoxide, whereas the $^1O_2$ reaction of (*Z*)-2-methoxy-2-butene (**47b**) provides both tertiary (63%) and secondary (38%) peroxides. A cis methoxy effect was observed in gas-phase $^1O_2$ reactions of these enol ethers. Dioxetane reactions were not observed in these systems. Since the activation barrier for the dioxetane formation of **46** and **47** is larger by at least 5 kcal mol^{-1} than that of the ene reaction, as shown in Table 5, this is reasonable. On the other hand, 2-methylpropene reacts with $^1O_2$ to give both hydroperoxide (88%) and dioxetane cleavage products (12%). Hammond[19] has explained his observation by assuming the Harding–Goddard biradical mechanism,[2] hence, anomeric stabilization of the peroxybiradical intermediate, requiring an overlap of the lone pair electron on oxygen with the C–OCH$_3$ bond, favors a conformation in which hydrogen abstraction from an allylic group cis to the methoxy substituent leads to a hydroperoxide. He has pointed out that his results are inconsistent with the perepoxide mechanism, which predicts H-abstraction from the methyl trans to the methoxy group. Since 2-dimethylpropene is 3-times less reactive than 1,1-dimethoxypropene, he has assumed that the C$_\beta$-attacked biradical (**48**) is more stable than the C$_\alpha$-attacked one (**49**). The former (**48**) returns to the reactants, or provides dioxetane, while the latter (**49**) provides the hydroperoxide, as outlined in Fig. 5. His results, however, can be alternatively explained by invoking different transition states for the $^1O_2$ ene and dioxetane reactions of enol ethers, as shown in Fig. 3. In fact, perturbation calculations[12] suggest that for this electron-rich system the oriented complex (**50**) instead of (**51**) could be formed before converting to the (2+2) TS (Chart 10). Thus, the ene reaction is highly suppressed by this directing effect, although the E_a-value is estimated to be very small. It is noteworthy that enamine DPA undergoes no ene reaction for the same reason.[22]

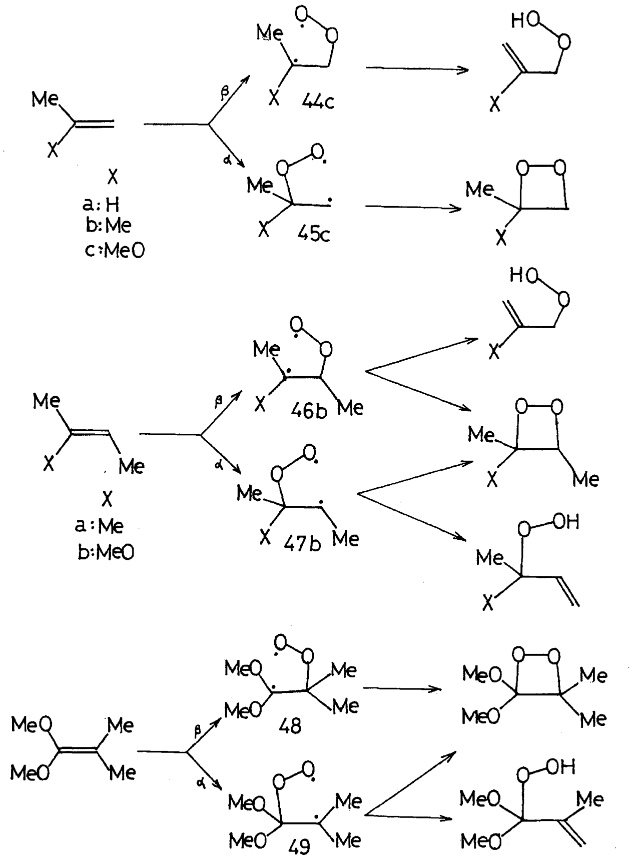
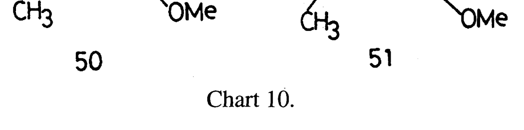


Fig. 5. Schematic illustrations of the regioselectivities for additions of $^1O_2$ to methyl- and methoxy-substituted olefins affording peroxy 1,4-biradicals (44—49). Paths α and β denote the α- and β-carbon attacks, respectively.

In summary, the computational results, together with the molecular-beam experiments[15] have provided the conclusions that: (i) the ene reactions of allylic olefins and enol ethers proceed through the model B TS even in the gas phase, and (ii) dioxetane-forming reactions of unsymmetrical olefins and enol ethers proceed through a different TS from the model B TS with a PE-like conformation. The ab-initio MO calculations[3,18] and activation energies in Table 5, together with Fig. 2 favor a BR TS for unsymmetrical olefins at a high temperature in the gas phase.

2. Solution-Phase Reactions of Unsymmetrical Olefins.

(A) Unsymmetrical Olefins: Perturbation calculations[12]



50 51

Chart 10.

have suggested that a π-complex with a charge transfer (CT) character is formed in singlet oxygen reactions in the solution phase. However, it is a subtle problem as to whether an exciplex is stabilized into perepoxide as a discrete intermediate or not in the solution phase, since it depends on the kind of substrates and solvation energies, as shown in Tables 1 and 4. Ab-initio calculations suggest that an allylic hydrogen interacts intramolecularly with the terminal oxygen to stabilize a model B TS with a PE-like conformation in an aprotic solution, because of no intermolecular hydrogen bonding. Therefore, theoretical calculations favor a nonradical mechanism via the model B TS for the ene reactions of allylic olefins, at least in an aprotic solution. Many available experimental results[10,11] seem to be consistent with this nonradical mechanism.[21]

Foote and Denny[6] have shown that solvent effects on the product-forming step for the ene reactions of 2-methyl-2-pentene and 2-methyl-3-(substituted phenyl)-2-butene are small, and that neither the charge or radical character is localized in the transition state (Chart 11). It has been found that although the ene reaction is very sensitive to the conformation of the hydrogen being transferred it is insensitive to substituents introduced at the *para*- and *meta*-positions. They proposed a concerted mechanism via a six-membered TS, like the model A TS for ene reactions of the allylic olefins. Similar conclusions have been obtained by Gollnick et al.[7] It is noteworthy that these classic data are compatible with the model B TS of the PE-like orientation. It is noteworthy that the model B TS is different from the PE intermediate with a partial ionic character. If ene reactions of allylic olefins proceed through the perepoxide-like TS or intermediate, they should be sensitive to the solvent polarity, as confirmed by an ab-initio calculation.[3] However, experiments have manifested no significant solvent effect for the ene reactions of allylic olefins.

Stephenson et al.[23] have carried out extensive experimental studies on the ene reactions of olefins, particularly the product distributions, product isotope effects and stereospecificity. It was shown that: (i) allylic hydrogens on the more crowded side are more reactive in trisubstituted olefins, the so-called *cis* effects; (ii) only a *cis*-substituent is responsible for the product isotope effect; and (iii) the ene reactions of alkenes are stereospecific. Their final conclusion is that ene reactions are concerted processes via π-complexes. Namely, they favor, instead of a perepoxide intermediate, a mechanism in which the frontier orbital interactions within a π-complex leads the system directly into an ene reaction. Their conclusions are consistent with the two-stage mechanism, namely a π-complex followed by the model B TS.[21]

Schuster et al.[27] have clearly demonstrated the important roles of charge-transfer interactions and exciplex (encounter complex in some case) formations at an early stage of the ene reactions of allylic olefins and cycloalkenes. Their experiments have revealed that an entropy-controlled process determines the relative rate of the ene reactions of these species in a CS_2 solution, as shown in Table 6 (so-called "cis" effect).[23—25] As illustrated by the orbital interactions, the model (B) TS with a PE-like conformation requires an axial conformation of the allylic hydrogen, which is not the most stable conformation for a reactant olefin, itself, as shown by Houk et al.[26] On the other hand, such a rigid geometry is not necessary for th exciplex (complex), where only the weak interaction between the π-lobes is crucial, as in the case of the π-complex formations between singlet carbenes and olefins.[34] Therefore, there should appear an energy barrier caused by the loss of the rotational freedom of the alkyl groups, which is the origin of the negative entropy, along the reaction path from the exciplex to the model (B) TS, in agreement with the isotope experiments by Stephenson et al.[23] and rotational energy barriers calculated by Houk et al.[26] We have proposed a two-stage concerted (TSC) mechanism[19] for the ene reactions in order to distinguish between the two stages, namely the model (B) TS and π-complex formations, which are the rate-determining steps in the cases **a** ($\Delta G > \mathrm{O}$) and **b** ($\Delta G < \mathrm{O}$),[27] respectively, as illustrated in Fig. 6. The TSC mechanism is compatible with both the spectroscopic results and well-established results by chemical means.[6,7,10] Thus, there is no uncertainty in the mechanism of the ene reactions of allylic olefins.

(B) Enol Ethers: There is much controversy concerning explanations of the singlet oxygen ene reactions of enol

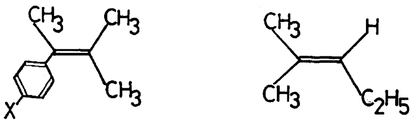


Chart 11.

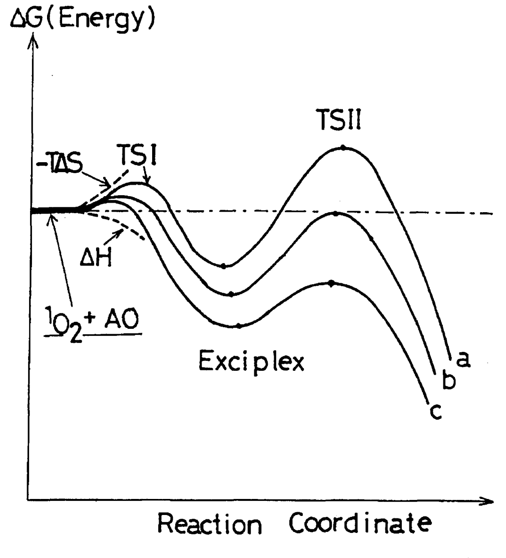


Fig. 6. Potential curves for the ene reactions between $^1O_2$ and allylic olefins (AO). TSI and TSII are the transition states for the exciplex formation and ene reaction, respectively. The dashed line shows the variation of the enthalpy and entropy terms for the initial step. a, b, and c denote the potential curves for weak, intermediate and strong donors, respectively.

ethers. This is not so surprising, since the BR, PE (or PEZW), and ZW intermediates are almost equally stabilized in polar solutions for the species, as shown in Tables 1 and 4; also a discrete intermediate would indeed be formed in the solution phase. Here, detailed examinations of both the theoretical and experimental results are presented.

Several mechanisms are presented to explain the cis methoxy effect for the ene reactions. Harding and Goddard[2)] have pointed out that their BR mechanism is applicable to explain the *cis* methoxy effect for the hydroperoxide formation observed by Conia et al.[35)] The (*E*)-1-methoxy-2-cyclopropylpropene (**17**) gave a 1 : 1 ratio of the hydroperoxide and dioxetane, while the trans olefin gave only 4% of the hydroperoxide and 96% of the dioxetane. However, Conia et al.[35)] and Frimer[10)] have pointed out that the ring-opening reaction of the cyclopropyl group, rather than 1-methoxy-1-hydroperoxy-2-isopropylidene propane, ought to be observed if a biradical center is indeed formed. Therefore, Conia et al.[35)] have considered that, instead of a BR, a *cis* zwitterion stabilized by the anomeric effect of the methoxy group undergo the ene and (2+2) reactions; the ratio of the ene to the (2+2) reaction is determined by the conformation of ZW. As shown in Table 1, the BR and ZW states are indeed nearly degenerate in energy in a less-polar solution, and the latter is the most stable in a polar solution. However, an ab-initio MO calculation[36)] suggests that the β-attacked ZW is more stable, due to an electron-donating property of the methoxy group, than the α-attacked ZW proposed by Conia et al.[35)] Therefore, it is hardly conceivable that an α-attacked ZW is a common intermediate for both the ene and (2+2) reactions of **17**.

The *cis* methoxy effects[35)] observed for *cis* isomers are similar to the *cis* effect observed for trisubstituted olefins. Namely, the *cis* effect cannot be attributable to the anomeric effect of the oxygen atom.[18)] These results indicate that attractive interactions, which favor a crowded conformation, should be operative. Therefore, *cis* effects are rather compatible with π-complex formations for alkenes and enol ethers. A two-stage mechanism[21)] may be operative for the ene reactions of the *cis* enol ethers. Since model B TS has a chair conformation, the *cis* effect observed for the *cis* olefins and enol ethers may be attributable to the rotational energy barrier to bring the allylic hydrogen at an axial position for the ene reaction.[26)] On the other hand, it seems reasonable that *trans*-isomers undergo (2+2) cycloaddition in the solution phase (Chart 12).

The calculated results given in Tables 1, 2, 3, and 4, together with recent laser experiments on the reactive quenching of $^1O_2$ in the solution phases,[9)] illuminate the characteristics of the profiles of the potential curves. The activation energies (E_a) for the ene reactions of the enol ethers are positive in sign in the gas phase, as shown in Table 6, suggesting that TSII in Fig. 6 is the rate-determining step. On the other hand, TSI might become the rate-determining step even for such systems in the solution phase, because Koch has observed a reduced E_a-value in methanol, as shown in Table 7.

Gorman et al.[9)] have reported striking evidence supporting exciplex formations between $^1O_2$ and enol ethers with allylic hydrogens. Table 7 summarizes the observed and calculated activation enthalpies and entropies. The calculated E_a values for the ene reactions of these species are 3—5 kcal mol^{-1} in the gas phase, whereas they are reduced to 0—2 kcal mol^{-1} if we subtract the solvation energy, about 3 kcal mol^{-1}, as shown in Table 7. The latter values are close to the observed values by Gorman et al. The exciplex formation TSI is the rate-determining step for the enol ethers, suggesting a nonradical mechanism passing through TSII, i.e., the model B TS, in Fig. 6. Since the CT character is small (10%) in the very early TSI, leading to π-complex formation, the solvent effect on the ene reaction rate should not be substantial,[12)] a prediction which is compatible with their experiments.[9)]

Further experimental support of the nonradical mechanism for the ene reactions is available. Bartlett and Schaap[37)] and Bartlett and Frimer[38b)] have investigated the ene and (2+2) cycloaddition reactions of cyclic enol ethers, and have presented the following results: (i) in the photooxidation of enol ethers, polar solvents favor cycloaddition, while nonpolar solvents favor ene product formation. However, the solvent effect on the ratio of ene to cycloaddition is much smaller than those seen in ionic cycloadditions. Namely, they are 34, 59, and 7 for **52**, **53**, and **54**, respectively, from nonpolar (benzene, cyclohexane) to acetonitrile (Chart 13). (ii) The higher value of the interaction with allylic hydrogen $H_c(T_c)$ in benzene (1.335) than in acetonitrile (1.211) reflects the greater dependence of the transition state on intramolecular hydrogen bonding in a less-polar solvent (iii). The simplest six-membered concerted ene mechanism (model A TS) is clearly ruled out because of the observed isotope effect for H_b (D_b,T_b) at position 5 (C_β). Namely, the O_1–C_β interaction is not negligible. (iv) The kinetic isotope effect for H_a at the C_α-atom is negligible, indicating that no rehybridization to sp^2 from sp^3 occurs at the position 6 (C_α). The model B TS satisfies all of the requirements in (i)—(iv): O_1–C_β bonding, O_2–H_c interaction and less ionic property. However, although an unsymmetrical (2s+1s) TS (model Q) to provide PEZW and (2s+2s) TS (model J) to ZW has an sp^2 carbon at position 6, there is a rehybridized carbon at posi-

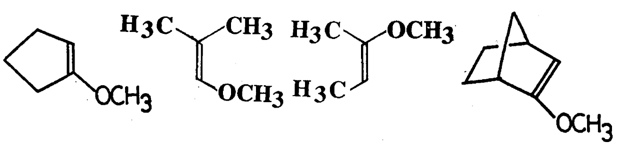
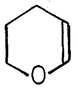


Chart 12.



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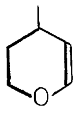

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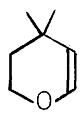

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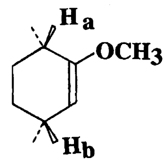

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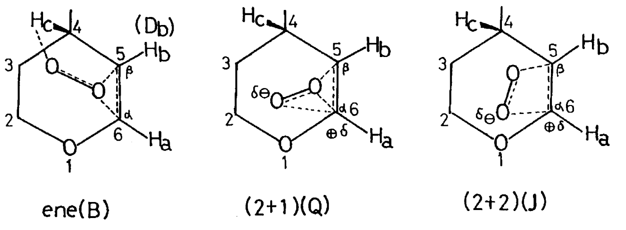
Chart 13.

Table 7. Activation Energies and Entropies, and Quenching Rates for Singlet Oxygen Reactions of Various Substrates

Substrates	I_p	ΔE_a [a]		$\Delta H^{\#}$ [b]	$\Delta S^{\#}$ [b]	k_q [b]	Solu. [b]	Modes [c]
	eV	Gas	Solu					
(*E*)-2-Butene	9.13	7.3		0.3	−42	7.2×10^3	C	ene
(*Z*)-2-Butene	9.13	6.5		1.6	−32	4.8×10^4	C	ene
(*E*)-3-Hexane	9.16			0.4	−39	7.7×10^3	C	ene
(*Z*)-3-Hexane				2.0	−31	3.9×10^4	C	ene
2-Methyl-2-butene	8.60	4.9	1.6	0.7	−30	2.4×10^5	C	ene
2,3-Dimethyl-2-butene	8.30	3.2	0.5	0.5	−23	2.2×10^7	C	ene
Cyclopentene	9.12	7.4		1.2	−32	5.8×10^4	C	ene
1-Methoxycyclopentene				−1.0	−30	1.2×10^7	T	ene
				−0.5	−27	2.5×10^7	A	ene
(*E*)-2-Methoxy-2-butene	8.2		3—5 [d]	−0.3	−28	1.2×10^7	T	ene
			1—2 [d]	−0.8	−27	2.4×10^7	A	ene
1-Ethoxy-2-methylpropene			3—5 [d]	0.2	−23	3.1×10^7	T	ene
			1—2 [d]	−0.3	−24	3.9×10^7	A	ene
1,3-Cyclopentadiene	8.58	3.9	0.25	0.0	−26	3.9×10^7	T	DA
Furan	8.89	5.3	0.2	0.0	−28	1.1×10^7	T	DA
2-Methylfuran		3.9	0.4					DA
2,5-Dimethylfuran				0.0	−20	6.8×10^8	T	DA
2-Methoxynorbornene			6—8 [d]			1.1×10^4	T	2+2
			0—2 [d]	−0.3	−34	6.2×10^5	A	2+2
1-Dimethylamino-2-methylpropene	7.5	2.6						2+2
Indole (ID)	7.79			0.0	−34	9.7×10^5	T	2+2
3-Methyl-ID	7.52			0.0	−29	9.2×10^6	T	2+2
3-Methyl-2-phenyl-ID				0.0	−27	2.1×10^7	T	2+2
2,3-Dimethyl-ID	7.30			0.0	−24	1.0×10^8	T	2+2

a) Activation energy (Ref. 13) for singlet oxygen reactions in gas and solution phases (solvent=methanol), b) activation parameters (Refs. 8 and 21) of the quenching of singlet oxygen by substrates in solution (solvents: C=(CS_2), T=toluene, and A=acetone), c) DA=(4+2) reaction, d) estimated values from Table 4.

tion 5 (Fig. 7). The former TS exhibits a relatively weak, but nonnegligible, O–H_c interaction, while the latter TS has no such interaction. This implies that the isotope effect on H_c becomes small in a polar solution, in accord with observation (ii) by Frimer et al.[38a] Since TS models Q and J have a moderate CT (about 25%) character,[12] the (2+2) cycloadditions should be accelerated in a polar solution, compared with the ene reactions via the model B TS. This is responsible for the change in the ratio of ene to (2+2) due to the solvent polarity, the observation (i) by Frimer et al.[38a] For example, **54** undergoes a concerted ene reaction to provide the hydroperoxide **55** (67%) in a nonpolar solution (Chart 14), because of the axial conformation of hydrogen, while the polar intermediates (PEZW,ZW) formed in a polar solution undergo a intramolecular proton-transfer reaction to provide the hydroperoxide **56**, and the (2+2) reaction to dioxetane.



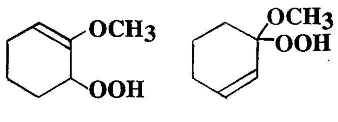
ene(B) (2+1)(Q) (2+2)(J)

Fig. 7. Proposed transition state for ene reaction (model B) and [2s+1s] (model Q) and [2s+2s] (model J) TS's for dioxetane-formation reaction.

Thus, the ene product ratio of **56** to **55**, together with the ratio of (2+2) to ene, increases with that of solvent polarity.

Wilson and Schuster[5b] favor a two-step mechanism via the PE intermediate for the ene reaction of **23** (which belongs to the type II species).[3] Namely, the π-complex is stabilized into a discrete PEZW intermediate, which undergoes intramolecular hydrogen abstraction. Judging from the solvation energies fro PEZW given in Tables 1 and 2, it is a difficult question as to whether π-complex moves directly to the model B TS, or collapses into a PE-like 1,4-dipole (PEZW). However, both mechanisms entail no difference in the regioselectivity for ene reactions of the enol ethers with allylic hydrogens.

(C) Olefins with Electron-Accepting and Donating Groups: There are tow extreme cases: (i) olefins with electron-accepting groups (**57**) and (ii) olefins with strong electron-donating groups, such as enamines. Recent experiments have documented that hydrogen abstraction occurs regioselectively at the alkyl group geminal to electron-with-

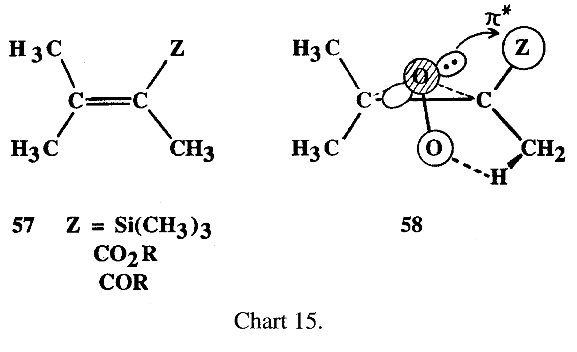


56 **55**

Chart 14.

drawing functional groups, such as aldehyde, keto, acid, and ester.[29—33] The same geminal regioselectivity was also observed for vinylsilanes and vinylstannanes.[3d] Since the electron-donating property decreases for these species, because of the electron-withdrawing groups, polar intermediates (PE, PEZW, ZW) should be less stable than the nonpolar BR intermediate in this type of olefin in the gas phase and a nonpolar solution. The activation energies for the ene and (2+2) reactions of these species were estimated, as in the case of the enol ethers (Table 5). Table 7 summarizes the calculated values. From Table 7, the (2+2) reactions are indeed unfavorable for the species, as expected, while the ene reaction via the model B TS is feasible, even in this case, although Adam et al.[30] have assumed a PE-like discrete intermediate, even for alkenes, which bears anion-stabilizing groups. The trapping experiments of the PE intermediates seem to be necessary to confirm the PE mechanism for electron-deficient olefins. Adam et al.,[30] Clennan et al.,[31] and Orfanopoulous et al.[32] have pointed out that the regioselectivity in these reactions cannot be fully explained by the rotational energy barriers of the allylic hydrogens,[26] and that electronic factors partly participate to control the stereochemistry. The π^*-orbital of the electron-accepting group may participate to stabilize the lone pair electron of the oxygen atom on the double bond in the model B TS (**58**) (Chart 15). Further detailed studies are, however, necessary for obtaining a full understanding of the gemi- and regioselectivities of the ene reactions of olefins with silyl groups.

Gorman et al.[9] have measured the rate constants of $^1O_2$ quenching by furans, indoles, and enol ethers. It was found that the activation enthalpies are nearly zero, or slightly negative in sign, whereas large negative activation entropies are obtained, as shown in Table 7. They have concluded that the observed results are consistent with the formation of exciplexes (oriented complexes in the excited state) at an initial stage of singlet oxygen reactions of these species. The large observed negative activation entropies were attributed to the rigid conformation required for the exciplexes. The exciplex should move to a concerted TS for the (4+2) reactions of furans to provide endoperoxides, since no trapping product is available. The situation is probably the same for the ene reactions of enol ethers with allylic hydrogens, as illustrated in Fig. 3. On the other hand, the laser techniques clearly demonstrated that the exciplexes are precursors for the polar intermediates of the (2+2) cycloadditions of enol ethers and indoles with $^1O_2$, as illustrated in Fig. 4.



57 Z = Si(CH$_3$)$_3$
CO$_2$R
COR

58

Chart 15.

Huisgen et al.[14] have also observed large negative entropies for the Diels–Alder reactions between dienes and olefins, and cyclobutanone formations between olefins and ketenes, as well as (2+2) cycloadditions of polar olefins. The former two reactions involve concerted (4s+2s) and (2s+2a) reaction paths, respectively, whereas the last corresponds to a two-step process via ZW intermediates. The large negative entropies are attributable to the formation of a rigid transition state, or an intermediate or complex, irrespective for the symmetry-allowed and -forbidden natures of the reactions. The $^1O_2$ reaction mechanisms via the model B TS or via ZW proposed for unsymmetrical olefins are therefore compatible with the closely related cycloaddition mechanisms of the dienes, ketenes and olefins.

In summary, a nonradical mechanism via the model B TS with a PE-like conformation is most plausible for the ene reactions of allylic olefins and enol ethers with allylic hydrogens in nonpolar and less-polar solutions. Many arguments which favor a perepoxide intermediate for the ene reactions are applicable to the π-complex, which is a precursor of the model B TS. The π-complexes have been detected by laser techniques. The conversion of a π-complex into σ-complexes (PE intermediate) is dependent on the electron richness of the substrate olefins and solvent polarity. A nonconcerted mechanism via polar (PEZW, ZW) intermediates is operative for the (2+2) cycloadditions of the unsymmetrical enol ethers in the solution phase. The ratio of (2+2) to the ene reaction should increase with increasing solvent polarity because of the moderate ionic character of the ZW (or PEZW)-like TS for (2+2) cycloadditions.

Mechanisms of Ene and (2+2) Reactions of Symmetrical Olefins

The addition reactions of $^1O_2$ to the C–C double bonds to afford perepoxides can be regarded as an electrophilic addition. Similarly, the additions of singlet atomic oxygen, nitrene, and carbene to the olefinic double bond all exhibit an electrophilic character, a property which is common for the addition reactions of cationic species. The transition states of these reactions are described by a three-center two-electron model.[1,39]

Laser photolysis experiments have established complex formation in the case of carbene additions to olefins.[40] In fact, the observed activation enthalpies are nearly zero, or slightly negative, while the activation entropies are largely negative. Thus, the general trends are the same for carbene[34] and singlet oxygen[21] additions to olefins.

Many experimental studies[39] have been conducted to elucidate the geometrical (cyclic or noncyclic) structures of the transition states for electrophilic additions. Browns[41] has presented a criterion that the ratio $k_{exo(\mathrm{NB})}/k_{exo(\mathrm{DNB})}$ of the rates of an exo addition to norbornene (NB) and 7,7-diethyl norbornene (DNB) is relatively high for additions involving cyclic transition states or intermediates (cyclic addition), and is relatively low for additions not involving cyclic transition states or intermediates (noncyclic addition). The k_r-value of epoxidation by peracid is 1000, whereas it is only 30 in the case of a •SPh radical addition. The transition state (TS) for the former reaction could be similar to that of the $^1O_2$ perepoxide mechanism by Dewar and Thiel.[1)] The TS for an •SPh addition, on the other hand, is close to that of the $^1O_2$ biradical mechanism by Harding and Goddard.[2)] Interestingly, the k_r-value is about 250. On the basis of this magnitude of the k_r-value we have concluded that the TS for $^1O_2$ ene reaction is a weakly "bonded" cyclic form, i.e., the model B TS with a PE-like conformation.[21)] This proposal is compatible with the conclusion for 2,3-dimethyl-2-butene by Stephenson et al.[23)] from experimental grounds.

By using ^1H and ^{13}C NMR spectroscopy, Olah[42)] has demonstrated that a bridged halonium ion structure is preferred for a symmetrically substituted olefin (group **III** and **IVs** olefins in our classification), whereas an open α-halo cation is formed for an unsymmetrically substituted olefin (group **I**, **II**, or **IVu** olefins in our classification). Therefore, an α bridged structure is also anticipated for norbornenes, compatible with the large k_r-values for ionic additions to the species. Judging from the k_r-value for $^1O_2$ addition, a concerted (2s+2a) mechanism via the π-complex has been proposed on the basis of a perturbation calculation for symmetrically substituted electron-rich olefins in nonpolar and less-polar solutions, as illustrated in Fig. 8.[12)] The concerted mechanisms require that the rate-determining step is each product-forming step.

Since the ionicity of the ene path (model B TS) is larger than that of the concerted (2s+2a) path, the former mode is rather accelerated in a polar solution than the latter in the case of group **III** olefins. Detailed experiments concerning this point have not yet been performed. The available data on the oxygenation reactions of 1,2-diphenylcyclobutene[43)] and stilbestrol[44)] are compatible with the theoretical results. The solvent effects for the ratio of ene to the (2+2) reaction are opposite between the unsymmetrical and symmetrical enol ethers.

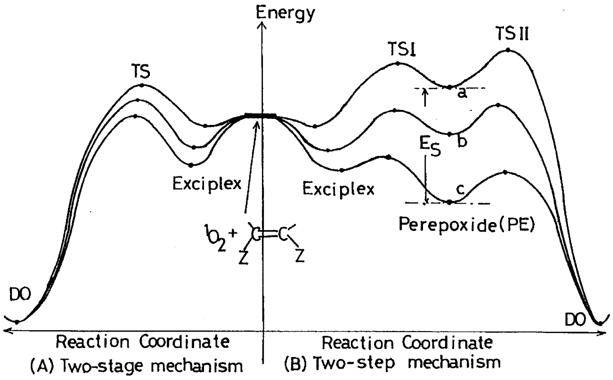
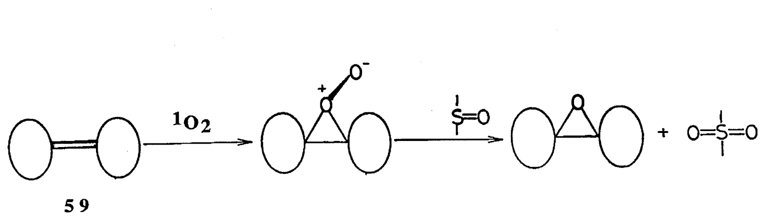


Fig. 8. Potential curves for the (2+2) reactions between $^1O_2$ and symmetrical olefins: (A) two-stage mechanism passing through the (2s+2a)-like TS via exciplex and (B) two-step mechanism passing through perepoxide (PE) intermediate. TSI and TSII are the transition states for perepoxide and dioxetane formations, respectively. E_S denote the solvation energy: a; gas phase, b; intermediate solvation and c; strong solvation.

The stabilization of the π-complex to a PE-like intermediate by Fukui et al.[45)] and perepoxide intermediate by Dewar and Thiel[1)] is a subtle problem, even for symmetrical olefins. The present results given in Table 4 show that it depends on the substrates and the solvations effects. From Table 4, the perepoxides are the most stable intermediates in protic solvents for symmetrical olefins. The ab-initio calculations have elucidated that the (2s+1s)-type TS to PE is more favorable due to the hydrogen-bonding stabilizations than the corresponding (2s+2s)-type TS to BR.[3e)] Thus, the solvation energies permit the formation of perepoxide as a discrete intermediate in protic solvents.

Schaap et al.[46)] have trapped the PE intermediate by diphenyl sulfoxide in the case of adamantylideneadamantane. They have shown that **59** undergoes (2+2) cycloaddition with $^1O_2$ to provide dioxetane in the absence of a trapping reagent, as illustrated in Fig. 8B, while dioxetane formation is drastically suppressed by the addition of sulfoxide to afford the corresponding epoxide (Chart 16). Saito et al.[8b)] have tried to trap the putative PE intermediate for the 1,2-diethoxyethylene or 2,3-dihydro-5,6-diphenyl-1,4-dioxin plus $^1O_2$ system by trimethylsilyl cyanide or diphenyl sulfide. However, their trapping experiments have failed, even in polar aprotic solutions. Their results rather support the concerted mechanism given in Fig. 8A, since ab-initio calculations indicate that the PE's are stabilized by the hydrogen bondings as discrete intermediates which have a long lifetime for the trappings. Furthermore, computations have shown that the PE-like TS should be very sensitive to the solvent polarity (Chart 17). No solvent effects for tetramethylethylene (ene) and 1,2-diethoxyethylene (cycloaddition) may also support the concerted (2s+2a) mechanisms via the exciplexes shown in Fig. 8A. These experimental results,[8b,46)] together with theoretical calculations,[1,3,21,45)] suggest that a conversion from the π-complex to PE becomes feasible along with an increase in the electron-donating properties of type **III** and **IVs** olefins.

Ab-initio MO calculations[3e)] have shown that (2s+2s) cycloaddition via zwitterion is ruled out for the symmetrical group **III** and **IVs** olefins, such as 2,3-dihydro-1,4-dioxin. Huisgen et al.[14)] have shown that dioxene does not react with



59

Chart 16.

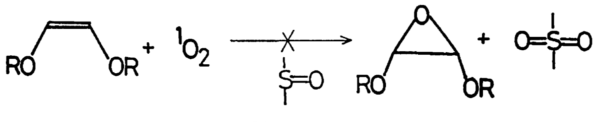


Chart 17.

tetracycanoethylene (TCNE); both the (2s+2s), (2s+2a) and (2s+1s) reactions are unfavorable, although the CT complex is truly formed between them. Previous perturbation calculations[12)] have suggested that although the (2s+2a) path between ethylene plus ethylene is unfavorable because of the large exchange repulsion, the same path between ethylene plus $^1O_2$ does not suffer such a large repulsion. Huisgen et al.[14)] have, furthermore, elucidated the greater reactivity of 1,1-dicyanoethylene with enol ethers than TCNE with the species. The experiments clearly show that the introduction of asymmetry is crucial for the (2s+2s) reaction passing through 1,4-zwitterion. Therefore, the classification of electron-rich olefins into symmetric (group **III** and **IVs**) and unsymmetric (group **I**, **II**, and **IVu**) ones is essential to understand $^1O_2$ cycloadditions as well as iso-electronic (2+2) reactions between polar olefins.

In summary, the (2+2) cycloadditions via ZW are unfavorable for symmetrical (**III**, **IVs**) olefins. The concerted (2s+2a) mechanism and two-step mechanism via the PE intermediate are conceivable for the (2+2) cycloadditions. Recent trapping experiments have indeed confirmed that the latter mechanism is operative for the (2+2) cycloaddition of adamantylideneadamantane.[46)] It is, however, not clear whether the same is true for other group **III** and **IVs** olefins. The present ab-initio calculations rather favor the former mechanism for these olefins, at least in less-polar and aprotic solutions. The failure of the trapping of PE and no solvent effect for the dioxetane formation of 2,3-dihydro-1,4-dioxin and 1,2-diethoxyethylene might support the calculated results. Similarly, a nonradical mechanism via the model B TS is reasonable for ene reactions of group **III** olefins with allylic hydrogens at least in nonpolar and less-polar solutions. The ratio of (2+2) to the ene reaction decreases along with an increase in the solvent polarity for group **III** olefins such as stilbestrol.[44)] This trend is opposite to that observed for unsymmetrical olefins. This, in turn, indicates that the dioxetane formation reaction proceeds through the less polar (2s+2a) TS.

Concluding Remarks

The reaction mechanisms of allylic olefins and enamines with singlet oxygen are relatively simple. The ene mechanism via the model B TS with a PE-like conformation and ZW cycloaddition mechanism via TS(J) in Fig. 7 are the most plausible, respectively. On the other hand, the mechanisms of the $^1O_2$ reactions of enol ethers should be complex in the solution phase, since the relative stabilities among the BR, PE(PEZW), and ZW intermediates are highly dependent on the substituents and solvent polarity, as shown in the relations A—G in Table 3. In fact, the obtained experimental results are diverse. However, the observed characteristics shown above are consistent with the trends derived from theoretical calculations of solvated TS and intermediates.

The ab initio and semiempirical results presented here, together with various experiments, indicate that the solvation and substituent effects, and molecular deformations accompanied by cluster formations with solvents, play important roles for transitions from neutral 1,4-biradicals (BR) to polar 1,4-zwitterions (ZW), and from π-complexes with a partial CT character to σ-complexes, perepoxides (PE) or PEZW, in singlet oxygen reactions. These effects were found to be essential for transitions from 1,3-biradicals to 1,3-dipoles (namely 1,3-ZW), and for reductions of the 1,3- and 1,5-BR characters for the transition states of 1,3-dipolar reactions.[3e,47)] The location of several transition structures stabilized with polar solvents by the ab initio energy gradient technique remains an important and interesting problem which will be solved elsewhere.

Concerning with the previous theoretical classification of 1,3-dipolar species (see Figs. 1 and 2 in Ref. 3e), we can easily understand the possible origins of the complex behaviors of the singlet oxygen reactions of enol ethers and enamines on the basis of the relative stabilities of the reaction intermediates summarized in Table 3. The 1,4-dipoles generated by $^1O_2$ reactions of these species often belong to the intermediate correlation regime (region II in Figs. 1 and 2 in Ref. 3e); therefore, their electronic properties should be sensitive to the environmental effects. In fact, the 1,4-BR character (region III) of the intermediates is predominant in the gas phase at high temperature, whereas the 1,4-ZW and PEZW characters (region I) are remarkable in polar solutions. A lot of the experimental results discussed here can be rationalized from the present MO-theoretical view point.[3)]

The present ab initio calculations were partly performed at the IMS computer center.

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