Tetrahedron Vol. 41, No. 11, pp. 2099 to 2107, 1985
Printed in Great Britain.

0040-4020/85 \$3.00 + .00

CHARGE-TRANSFER INTERACTIONS, EXCIPLEX FORMATIONS AND IONIC DISSOCIATIONS IN SINGLET OXYGEN REACTIONS

K. YAMAGUCHI,* Y. IKEDA and T. FUENO
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

(*Received in Japan* 18 *April* 1984)

Abstract—Intermolecular perturbation and configuration interaction calculations have been carried out to elucidate the attacking modes of singlet molecular oxygen ($^1O_2$) to allyl olefins and electron-rich olefins, which are classified into four groups from their molecular structures. It is found: (1) that the attacking modes are dependent on the molecular structure of substrates; (2) that the charge-transfer (CT) interactions between $^1O_2$ and substrates are particularly important for the formation of exciplexes through which the ene and (2 + 2) reactions of $^1O_2$ proceed; and (3) that the CT energy levels are important in governing the fraction of ionic dissociation to produce superoxide anion and the relative ratio between the (4 + 2) and (2 + 2) reactions of $^1O_2$ with dienes, heterocycles and related species.

A large number of experimental results have been accumulated on the reactivities, stereochemistry and other characteristics of chemical reactions between $^1O_2$ and various types of organic compounds.[1-7] These results reveal three different reaction modes providing endoperoxides, dioxetanes (or carbonyl fragments) and allylic hydroperoxides. The stereochemical data and other evidence available indicate that several reaction mechanisms may be operative in each reaction mode. One is the so-called concerted reaction which proceeds without well-defined intermediates, while other three mechanisms are such that the reaction proceeds stepwise via homopolar diradical (DR), zwitterion (ZW) or perepoxide (PE) as an intermediate. Furthermore, oxygenation reactions via charge-transfer (CT) complexes are conceivable on the basis of several pieces of circumstantial evidence. The charge-transfer could be of great importance since it permits participation of the ground state (triplet) molecular oxygen in type II-like reactions, which are usually considered to be characteristic of singlet oxygen. Clearcut distinction between singlet and triplet molecular oxygen reactions is of considerable difficulty in such cases. Therefore, researchers have begun to invoke singlet oxygen, but also triplet oxygen and superoxide anion, or its conjugate acid, the hydroperoxy radical, as the reactive oxygen species in oxygenation reactions of electron-rich species.

Theoretically, reacting complexes between molecular oxygen and organic compounds are regarded as a typical quasidegenerate system.[8] In other words, such complexes yield various electronic states with different characteristics which are, nevertheless, nearly degenerate in energy. This permits facile interconversion of reaction mechanisms or pathways upon a charge in reaction condition. Thus, we have carried out theoretical studies to elucidate important factors which govern the mechanism of oxygenation reactions.[9] These calculations have revealed an important role played by the CT interaction in determining the initial approach of $^1O_2$ toward substrates. As a continuation of previous work,[9] we here re-emphasize crucial roles of the CT interactions, exciplex formations and ionic dissociations in molecular oxygen reactions of organic substrates.

Intermolecular perturbation and configuration interaction calculations

Allylic and electron-rich olefins are classified into four groups from their molecular structures for elucidation of the mechanisms of their ene and (2 + 2) reactions with $^1O_2$.[9,10] (I) Olefins with the allylic hydrogens and electron-donating groups on the same side,[11] e.g. 2-amino(methoxy)propene [$CH_3ZC{=}CH_2$ ($Z = NH_2$, OCH_3)]. (II) Olefins with the allylic hydrogens on one side and with electron-rich groups on the other,[11-14] e.g. 1-amino(methoxy)propene [$CH_3CH{=}CHZ$ ($Z = NH_2$, OCH_3)]. (III) Olefins with allylic hydrogens and electron-donating groups (Z) on both sides in a symmetric manner,[15,16] e.g. stilbestrol [$CH_3ZC{=}CZCH_3$ ($Z = PhOCH_3$)]. (IV) Olefins without the allylic hydrogen.[17-19] These are classified into symmetrical olefins, e.g. 1,2-dimethoxyethylene [($CH_3OCH{=}CHOCH_3$)] and unsymmetrical olefins, e.g. 1,1-diaminoethylene [$(NH_2)_2C{=}CH_2$]. These are referred to as IV_s and IV_u groups, respectively.

Mulliken and Murrell-type perturbation theory[20-22] has been applied to several reaction-path models (A–P) of the above olefins. 2-Aminopropene, an example of group I, was analysed as depicted in Fig. 1.[9,10] Models D and F are similar to models B and A, respectively, previously discussed for the ene reaction of propene.[9] In model D, $^1O_2$ simultaneously attacks the allylic hydrogen and the centre of the C_α–C_β double bond. Models E and G are the (2s + 2s)-type approaches with symmetric (side on) and unsymmetric (end on) configurations of the reaction centres, respectively. The interaction energies calculated by the perturbation theory are given in Table 1 and indicate that, while both

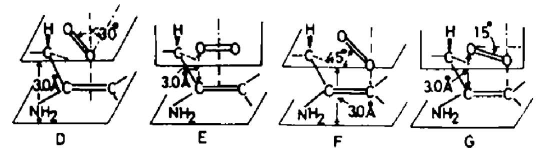


Fig. 1. Approach models for the perturbation calculations. Models D and F correspond to ene reaction paths for the 2-aminopropene plus $^1O_2$ system, whereas models E and G are symmetric and unsymmetric (2s + 2s) paths.

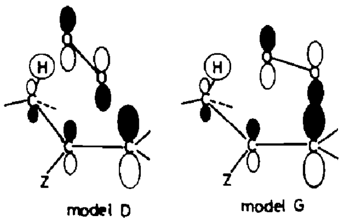
Table 1. Intermolecular interaction energies for various approach models[a] (kcal/mol) calculated by the Murrell perturbation theory[b]

System	Approach model	E_Q	E_K	E_I	E_D	E_{CT}	E_{total}
Propene + O_2	A	−0.27	0.61	0.00	−0.44	−0.66	−0.76
	B	−0.49	0.96	0.00	−0.54	−1.36	−1.43
	C	−0.22	0.56	0.00	−0.31	−0.55	−0.52
2-Aminopropene + O_2	D	−0.48	1.03	−0.03	−0.73	−1.34	−1.55
	E	−0.21	0.62	−0.06	−0.68	−0.32	−0.64
	F	−0.27	0.66	−0.04	−0.69	−0.64	−0.98
	G	−0.55	1.40	−0.09	−0.94	−1.81	−2.00
1-Aminopropene + O_2	H	−0.49	1.02	−0.00	−0.77	−1.39	−1.64
	I	−0.53	1.38	−0.03	−0.92	−1.23	−1.32
	J	−0.59	1.47	−0.05	−0.98	−1.53	−1.66
Ethylene + ethylene	K	−0.91	5.12	0.00	−0.75	−0.65	2.82
	L	−3.27	9.28	−0.00	−0.69	−1.26	4.05
Ethylene + O_2	M	−0.16	0.54	0.00	−0.30	−0.15	−0.07
Ethylene + ketene	N	−0.95	4.74	−0.01	−0.60	−1.37	1.82
cis-Propenyl ether + ketene	O	−1.60	6.82	−0.02	−1.01	−1.42	2.77
	P	−0.80	4.79	−0.02	−0.83	−1.15	2.00

[a] E_Q, Coulomb energy; E_K, exchange energy; E_I, inductive energy; E_D, dispersion energy; E_{CT}, charge-transfer energy.

[b] Refs 9 and 21.

G and D are of lowest energy, model G is preferred over model D because of the substantial asymmetry of the HOMO of 2-aminopropene. Thus, a (2s + 2s) pathway is more favourable than a concerted ene path in the case of electron-rich group I olefins. It should be noted, however, that both a (2s + 2s) cleavage reaction affording carbonyl fragments and the ene reaction occur and pass through zwitterions,[9] as can be seen from the reaction scheme for group I olefins illustrated in Fig. 2.[23,24]



The intermolecular CI results in Table 2 show that the electronic structure of a zwitterion is given by:

$$ {}^1\Phi_{ZW} = C_0\,{}^1A({}^1D\cdot{}^1O_2) + C_1\,{}^1CT_1({}^2D^{+}\cdot{}^2O_2^{-}) + C_2\,{}^1C({}^1D^{*}\cdot{}^1O_2). \quad (1) $$

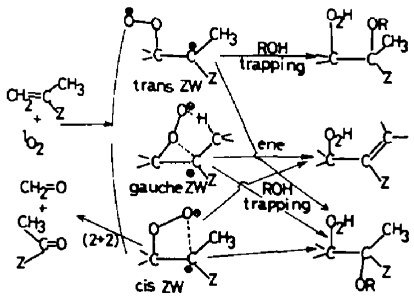


Fig. 2. Schematic illustration of the reaction scheme for ${}^1O_2$ ene and (2 + 2) reactions of electron-rich group I olefins (see text). *Trans*, *cis* and *gauche* refer to the conformations of zeitterionic (ZW) intermediate.

The electronic structure of an exciplex is described by the superposition of the ground ${}^1A$ and ${}^1CT_1$ configurations, where the weight of the latter is estimated to be *ca* 25% at the intermolecular distance $R = 2.5$ Å. The contribution of the locally excited (LE) configuration, which is responsible for the inductive energy, is small at $R = 2.5$ Å, but it increases at a shorter intermolecular distance through the back CT (BCT) from CT_1 as illustrated by Scheme 1. Therefore, there are activation barriers for the conversion of an exciplex to a zwitterion unless the stabilizations by the CT_1 interaction are sufficiently large, as illustrated in case (a) of Fig. 3.

The 1-aminopropene plus ${}^1O_2$ was examined by Mulliken and Murrell perturbation theory as an example of group II olefins. Models H, I and J, illustrated in Fig. 4, were examined.[9] Model H is the ene-type path, whereas I and J are the (2s + 2s)-type paths. The calculated results in Table 1 show that J is more favourable than I. Therefore, the regioselectivity observed for the ${}^1O_2$ addition to 1-aminopropene appeared in the (2s + 2s)-type approach model because of the moderate asymmetry of the HOMO of 1-aminopropene. The energy difference between J and H is minor, but it can increase in polar solution because of

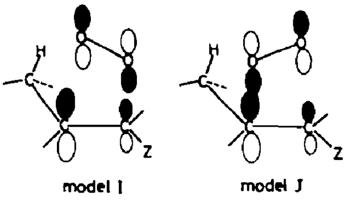
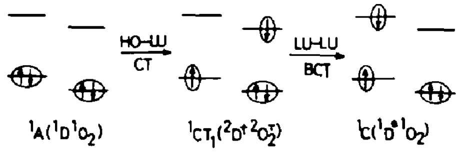


Table 2. Intermolecular CI results for propene plus $^1O_2$ system (I) and 2-aminopropene plus $^1O_2$ (or $^3O_2$) system (II)

System	State	E^b_{int}	CI coefficients[a,g]				
			$^{1,3}A$	$^{1,3}F$	$^{1,3}CT_1$	$^{1,3}D$	$^{1,3}CT_2$
I[c]	$^1\Delta$	−0.31	0.950	0.008	−0.313	—	0.008
	$^3\Sigma^e$	−0.12	0.984	—	0.178	—	0.005
II[d]	$^1\Delta$	−0.91	0.872	—	0.488	0.037	—
	$^3\Sigma^e$	−0.39	0.945	0.042	−0.323	—	—
	$^3\Sigma^f$	−0.43	0.935	0.046	−0.351	—	—

[a] The notations of configurations are given in Schemes 1 and 5.
[b] Interaction energy (eV).
[c] Approach model B in Fig. 1.
[d] Approach model G in Fig. 1.
[e] $^3CT_1 > {}^3F$ case.
[f] $^3CT_1 < {}^3F$ case, where an intermediate solvation, $E_S = 39$ kcal/mol was assumed.
[g] —, CI coefficient is smaller than 0.002.



Scheme 1.

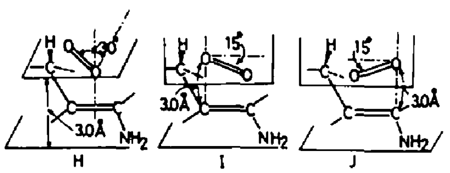


Fig. 4.

the large CT character of the former. The concerted ene and C–C cleavage reactions would be competitive in non-polar solution, whereas the relative amount of C–C cleaved product may increase in polar solution since the ene reaction is impossible in the model J approach. Thus, these perturbation calculations predict the reaction schemes for group II species shown in Scheme 2.[9]

These results are compatible with recent careful experiments on group II compounds, particularly 1-methoxycyclohexene by Bartlett and Frimer,[25] 4-methyl-2,3-dihydropyrane by Frimer *et al.*,[26] 1-ethylthio-2-ethylhexene-1 by Ando *et al.*[14] and 2,5-dimethyl-2,4-hexadiene by Hasty and Kearns.[27]

The asymmetry of the HOMO is crucial for the zwitterionic (2s + 2s) reactions of group I and II compounds. For group III, however, the HOMO is symmetric. Therefore, the (2s + 2a) reaction path is worthy of consideration for group III, as illustrated in Fig. 5. Both the (2s + 2s) (model K) and the (2s + 2a) (model L) approaches of two ethylenes were examined, as shown in Table 1. The large exchange repulsion energy prevents the (2s + 2s)-type dimerization of ethylene. However, its (2s + 2a) dimerization of ethylene is also unfavourable. The perturbation calculation predicts large activation energies for (2s + 2a) cycloadditions between olefins. The (2s + 2a) approaches between ethylene and ketene (model N), and between *cis*-propenyl methyl ether and ethylene (models O and P) were also examined as shown in Fig. 5.

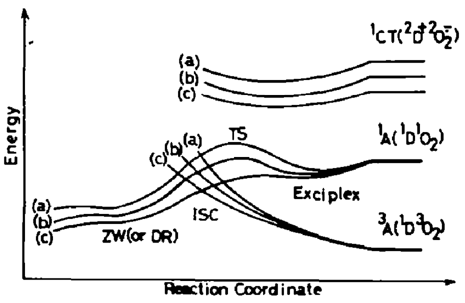


Fig. 3. Potential energy curves for (2s + 2s)-like approaches between $^1O_2$ and donor olefins, TS indicates the transition state and ISC denotes the points of intersystem crossing. Cases a, b and c are the cases of weak, intermediate and strong electron donors, respectively. Some examples are given in the text. Relative stability between DR and ZW are dependent on the CT energy levels and solvation energy.

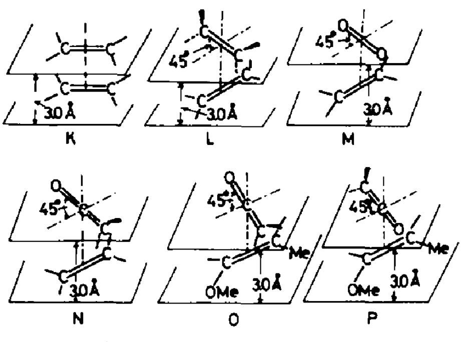
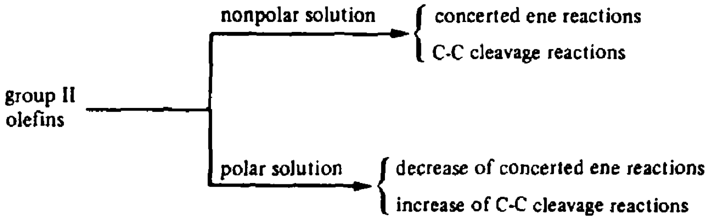


Fig. 5. Approach models for the perturbation calculation of the ethylene plus ethylene (K and L) and the ethylene plus $^1O_2$ (M) systems. Model K is the (2s + 2s) path, whereas models L and M denote the (2s + 2a) paths.



Scheme 2.

From Table 1, the total interaction energies for both cases are still repulsive since the exchange repulsion forces are exclusively large. The relatively small exchange repulsion prefers the anti conformation of ketene to *cis*-propenyl methyl ether (model P). The CT forces are weak since the intermolecular orbital overlaps between the HOMOs are not particularly large. Therefore, deformations of the reactants should be necessary for both an increase in the CT interaction and a decrease of the exchange repulsion. Such deformations are relatively easy for ketenes and cumulens, leading to concerted (2s + 2a) reactions.

The exchange repulsion is largely reduced for the (2s + 2a) approach (model M) between ethylene and $^1O_2$, but the CT attraction is also small. This implies that the (2s + 2a) cycloaddition becomes feasible if the electron-donating ability of donor olefins is substantial. Thus, perturbation calculations predict both concerted ene and (2s + 2a) reactions for group III compounds (Scheme 3).[9] In the case of group III olefins, since the ionicity of the concerted ene path (models B, D and H) is larger than that of the concerted (2s + 2a) path,[9] the former mode is favoured in polar solution over the latter. Detailed experiments on this point have yet to be performed. Nevertheless, the available data on the oxygenation reactions of 1,2-diphenylcyclobutane,[15] stilbestrol[16] and its analogues are compatible with the theoretical results.

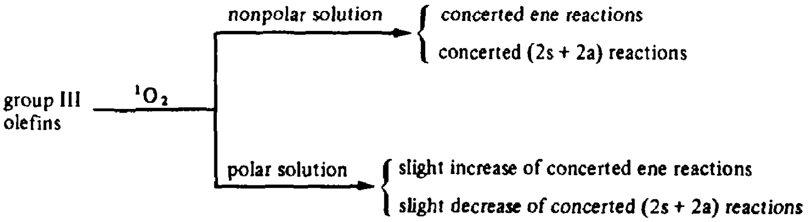
From the above results, the selection rules for olefins of group IV are those shown in Scheme 4.[9] The perturbation calculation would seem to prefer the concerted (2s + 2a) path for singlet oxygen reactions of 1,2-diethoxyethylene,[17] tetramethoxyethylene[18] and other symmetrical electron-rich (group IV_s) compounds. For unsymmetrical electron-rich (group IV_u) species, such as 1,1-diaminoethylene, (2s + 2s) C–C cleavage reactions passing through zwitterions are preferred, in conformity with various experimental results.[1–6]

Bartlett and Schaap[17] have proposed the concerted (2s + 2a) path for the dioxetane formation reaction of *cis*- or *trans*-1,2-diethoxyethylene because of the retention of configuration. On the other hand, a perepoxide mechanism has been considered for the singlet oxygen reactions of adamantylideneadamantane[28] and adamantylidenecamphene.[29] However, the results of the perturbation calculation suggest that a concerted (2s + 2a) mechanism for dioxetane formation may be operative for these olefins as well. The complex results[6,28,29] reported for these systems might indicate the partial involvement of sensitized type I photo-oxidation reactions. In fact, the 1,2-cation migration, which is allowed for the cation centre of peroxy cation radical, is observed in some cases.[6,29]

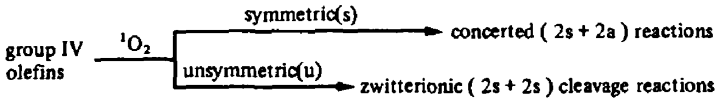
Let us close this section with a brief discussion of oxygenations by the ground state molecular oxygen.[30–33] From Table 2, the intermolecular CI wave-function of 2-aminopropene plus $^1O_2$ is approximated by Eq 2:

$$^3\Phi_{CX} = C_0\,{}^3A(^1D\cdot{}^3O_2) + C_1\,{}^3CT_1(^2D^{+\cdot}\,{}^2O_2^{-\cdot}) + C_4\,{}^3F(^3D^*\cdot{}^3O_2) \quad (2)$$

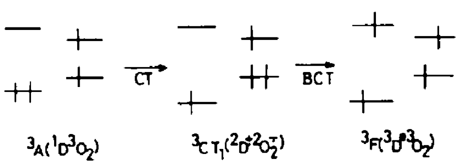
where the configurations are illustrated in Scheme 5. The contribution of $^3CT_1$ is significant, and that of ^3F is not negligible, indicating that the triplet excitation of



Scheme 3.



Scheme 4.



Scheme 5.

the donor is induced through the CT_1. The latter contribution increases in the case of electron-rich olefins[31] and acetylenes,[32] for example adamantylidene derivatives,[33] cyclic acetylenes and ketenes. Therefore, the 1,4-diradical formation through the ^3CT complex is thermally accessible for these systems, as in the case of autoxidations of monoanions of phenols and indoles.[9] The mechanisms of the CT followed by the spin inversion (CTSI) is shown in Scheme 6 (see also Fig. 3).[9,30] The spin inversion (SI) should be rapid in the case of the CT complex, for which the singlet and triplet spin states are quasi-degenerate in energy.

In summary, the end-on approach of $^1O_2$ to a electron-rich double bond of groups I, II or IV_u is energetically allowed to give a zwitterion (models G and J in Figs 1 and 4) which is trapped by alcohol and other trapping reagents. On the other hand, a (2s + 2a)-type concerted path to provide dioxetane is favourable for group III and IV_s olefins. Thus, the perturbation calculations indicate that the reaction modes of $^1O_2$ are highly dependent on the exact types of olefins.[9]

CT mechanism for singlet oxygen reactions

Estimations of weight of CT configurations. The perturbation and configuration interaction calculations revealed the crucial roles of the CT_1 interactions in determining the reaction paths of $^1O_2$ reactions since the transition states are early, i.e. reactant-like.[6] Therefore, an empirical method to estimate the CT_1 interaction between $^1O_2$ and aromatic molecules is of particular interest in this regard. In this section, such a method is considered and will be applied to calculate the CT character of the $^1O_2$ reaction intermediates of phenols, aryl amines and heteroaromatics.

The $^1CT_1$ configuration (Scheme 1), i.e. ion radical pair, is less stable than the dative configuration (^1A) for phenol and methoxybenzene derivatives at a relatively large intermolecular distance (R): $R > 3.0$ Å. Therefore, the formation of free superoxide anion is highly endothermic in these systems if $^1O_2$ is a true reacting species. However, the ^1CT configuration is stabilized with the decreasing intermolecular distance because of the increase in the electron-hole Coulombic attraction (J_{AD}),[20] whereas the dative structure ^1A is destabilized by the increase in exchange repulsion. Therefore, the $^1CT_1$ and ^1A configurations can be nearly degenerate in energy at a relatively shorter intermolecular distance. In such a case, the true singlet state of excited complexes (exciplexes) should be described by the superposition of both these configurations[20]

$$^1\Phi_{EX} = C_0\,{}^1A + C_1\,{}^1CT_1 \tag{3}$$

where C_0 and C_1 are given by solving the secular determinant. The ground state stabilization energy E^-_{total} and the CT excitation energy ΔE_{CT} are given as the function of $(\gamma + E_S)$ as follows:[34]

$$E^{\pm}_{total} = \tfrac{1}{2}[(\gamma + E_S) \pm \sqrt{(\gamma + E_S)^2 + 4W^2}] \tag{4}$$

$$\Delta E_{CT} = \sqrt{(\gamma + E_S)^2 + 4W^2} \tag{5}$$

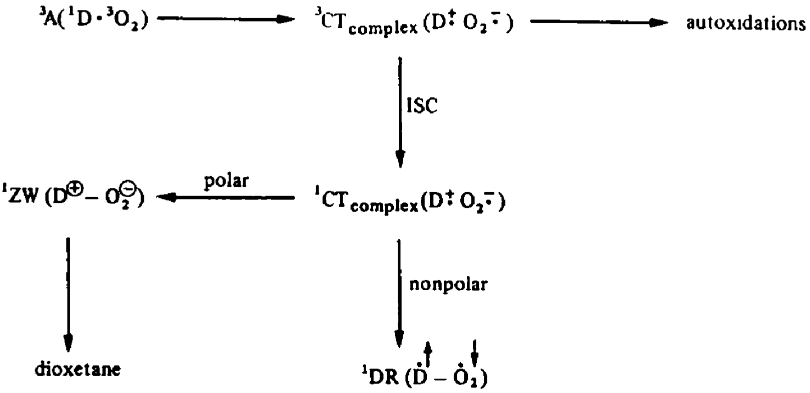
where E_S is the solvation energy for the CT_1 configuration. The energy difference (γ) between the ^1A and $^1CT_1$ configurations is approximately given by

$$\gamma = Ip - E_A - J_{AD} \tag{6}$$

Ip and E_A are the ionization potential of donor and electron affinity of acceptor, respectively. The interaction term (W) between the ground and CT_1 configurations, is proportional to the intermolecular orbital overlap.[22] The stabilization energy E^-_{total} is larger when the solvation energy E_S is large and the γ-value is small. For a large E_S and small γ, $|E^-_{total}|$ may well become large enough to outweigh the exchange repulsion energy. As a consequence, an intermediate with a strong CT character may be formed, where the CT character (x_{CT}) is defined with the weight of the CT_1 configuration in Eq 3 as follows:

$$x_{CT} = C_1^2. \tag{7}$$

The functional dependences of $E^{\pm}_{total}$, ΔE_{CT} and x_{CT} on $(\gamma + E_S)$ are depicted in Figs 6 and 7, where some important donors are marked by using the semi-empirically determined ΔG $(= \gamma + E_S)$ values.[34,35]



Scheme 6.

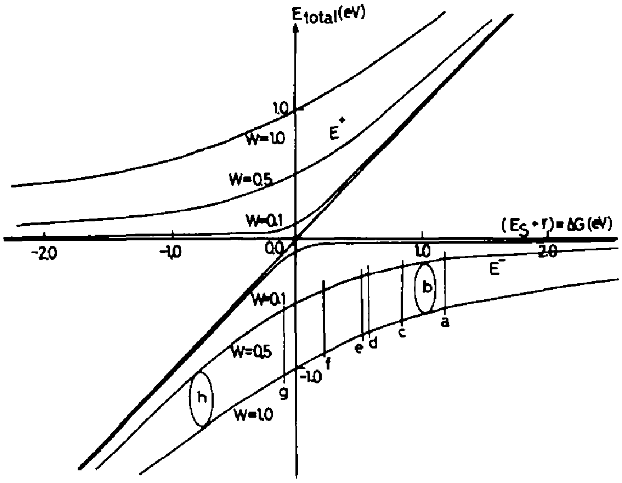


Fig. 6. Plot of the variations of the potential energy curves (Eq. 9) for charge-transfer systems with the diabatic energy difference ($E_S+\gamma$) between the ground ^{1}A and CT_1 configurations. The value W is the off-diagonal (interaction) term between these configurations. Some typical systems are presented: (a) dimethoxybenzene (DMB); (b) 2,4-di-t-butylphenol indole, tryptamine and tryptophane; (c) 2,4,6-triphenylphenol; (d) tetramethoxybenezene (TMB); (e) α-tochpherol; (f) dimethylaminoanisole (DAN); (g) NADH; and (h) flavin derivatives.

Phenols and methoxybenzenes. Figure 3 illustrates a plausible potential curve for the type II oxygenations of phenol derivatives passing through excited singlet complexes having a strong CT character. The CT character of exciplexes can exceed 40% in the case of electron-rich phenols, as shown in Fig. 7. For these complexes, proton transfer (PT) reactions characteristic of a CT_1 configuration are probable although, frequently, the free radical pair can rapidly recombine within the solvent cage as outlined in Scheme 7. There should be an activation barrier to the PT reaction, as illustrated in Fig. 3, which is accompanied by the back CT interaction from the CT_1 configuration. This implies that the quenching rate of $^1\mathrm{O}_2$ is proportional to the CT_1 interaction, whereas the PT rate is determined by the higher order interactions; namely local excitation of phenol derivatives.

Thomas and Foote[36] have demonstrated that the quenching rate of $^1\mathrm{O}_2$ is proportional to the oxidation potentials of phenol derivatives, suggesting that a CT mechanism is operative for the quenching reaction. They showed that the CT character for the transition state of quenching is *ca* 44% in the case of triphenyl phenol. However, the fraction of type II reaction giving quinone derivatives is very small, compared with quenching of $^1\mathrm{O}_2$, but the formation of the hydroperoxydienone through the exciplex (Scheme 7) is minor.[36] These results imply that the barrier height for the PT step is not negligible.

The (4 + 2) reactions between aromatic compounds and $^1\mathrm{O}_2$ are symmetry-allowed. However, mono- and disubstituted benzenes, such as phenol and dimethoxybenzene (DMB), do not undergo the reactions, indicating that the CT interactions in these cases are not sufficient to overcome the activation barriers, although they are sufficient to quench $^1\mathrm{O}_2$.[2] On the other hand, the (4 + 2) reactions do occur with the more electron-rich catechol and methoxybenzenes, such as 1,2,3,4-tetramethoxybenzene.[2,36] The CT mechanism is applicable to these cycloadditions, first, because the CT energy levels calculated for the methoxybenzene derivatives are very low[35] and, secondly, because the transition state for the (4 + 2) reaction is early.

Aromatic amines and heteroaromatics. The (2 + 2) reactions between aromatic compounds and $^1\mathrm{O}_2$ are symmetry-forbidden. However, unsymmetrical aro-

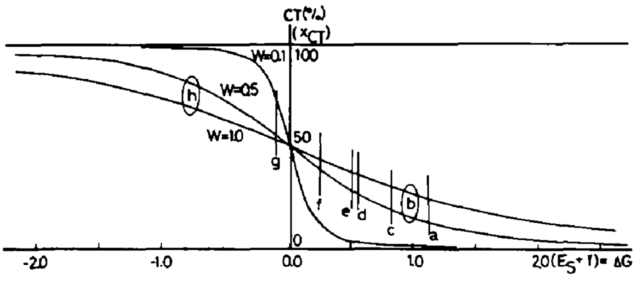
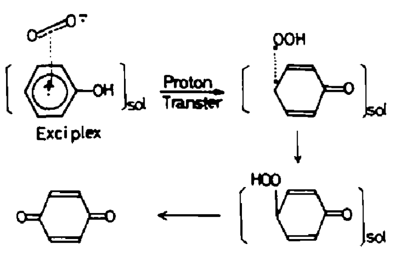


Fig. 7. Plot of the variations of the calculated CT character (x_{CT}) with the charge-transfer energy $\Delta G (= E_S+\gamma)$. The notations (a)–(h) are the same as in Fig. 6.



Scheme 7.

matic amines (having enamine moieties) have lower Ips and undergo (2+2)-type reactions in polar solution, providing the C–C cleaved compounds.[2] These reactions may proceed through exciplexes in non-aqueous solution.

The ionic dissociations and formations of superoxide anion are very important primary processes for some singlet oxygen reactions.[37] The free energy change for the production of the ionic pair $D_S^{+\cdot}$ and $A_S^{-\cdot}$ in acetonitrile (*S*) is given by Eq 8, which is similar to Eq 6:[38]

$$\Delta G_{IR}[DA]_S^{obs} = E_{1/2}(D/D^{+\cdot})_S - E_{1/2}(A^{-\cdot}/A)_S - e^2/a\varepsilon \quad (8)$$

$E_{1/2}(D/D^{+\cdot})$ and $E_{1/2}(A^{-\cdot}/A)$ are the oxidation potential of donor and the reduction potential of acceptor in solvent *S*, respectively. The last term is the Coulombic term which is 0.06 eV in MeCN ($\varepsilon = 36.7$) at $a = 7$ Å. In such a case the free energy change of the ion radical formation for the $^3O_2$-1,4-dimethoxybenzene (DMB) pair, $E_{ox}(DMB/DMB^{+\cdot}) = 1.34$ V SCE in MeCN, is calculated to be 2.10 eV.[35,37]

As seen from the oxidation potentials,[35] the ionic dissociation producing free superoxide anion is slightly endothermic in the case of electron-rich amines, such as tetramethylparaphenylenediamine (TMPD), diaminobutadiene and tetra-aminoethylene (TAME). Saito *et al.*[39] have demonstrated that the N,N-dimethylaminoanisidine (DAN)-$^1O_2$ system undergoes ionic dissociation in aqueous solution. However, the percentages of superoxide anion formed were only 1.1% for DAN, 6.5% for TMPD and 0.3% for N,N-dimethyl-*p*-toluidine ($E_{ox} = 0.65$ V SCE). The ionic dissociations for DAN and TMPD become negligible in non-aqueous solutions of MeOH and MeCN, in line with the endothermicity.[35,39]

By using the laser-flash photolysis technique, Peters and Rogers[140] have investigated quenching reactions of $^1O_2$ by the reduced form of nicotinamide adenine dinucleotide (NADH) and its analogues. The ion dissociation is exothermic by *ca* 0.40 eV in H_2O, as illustrated in Fig. 7 and, in contrast to TMPD and DAN, the dissociation was facile even in an organic solvent such as MeOH–MeCN. The extent of chemical quenching giving $O_2^{-\cdot}$ was *ca* 60% in this case. This efficiency is far greater than that obtained for aryl amines such as TMPD and DAN.

In conclusion, the CT character and CT energy level play essential roles in characterizing: (1) quenching reactions of $^1O_2$; (2) cycloadditions between electron-rich aromatic compounds and $^1O_2$; and (3) ionic dissociations into donor cation radicals and $O_2^{-\cdot}$. The CT characters for other electron donors are estimated by using Fig. 7 and the CT levels.[35]

CT control of $^1O_2$ reaction modes

The intermolecular CI (ICI) calculations have revealed the important role of the CT_1 energy levels in controlling the relative ratio between the symmetry-allowed and -forbidden cycloadditions.[9,10] In fact, the relative ratio of symmetry-forbidden (2+2) and -allowed (4+2) reaction paths for diene–olefin systems are highly dependent on the CT energy levels. Epiotis[41] has been first to formulate the ICI scheme for the (2+2) reactions between donor olefins and TCNE, and has emphasized the important role of CT_1 configuration, for which the (2+2) reaction is symmetry-allowed.

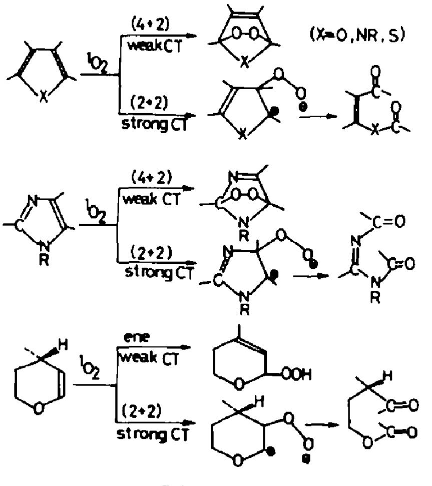
Similar conversions of the reaction modes have been observed for singlet oxygen reactions with heterocycles and electron-rich olefins bearing allylic hydrogens (Scheme 8).[2]

$$\delta = \frac{(2+2)\text{ reactions}}{(4+2)(\text{or ene})\text{ reactions}} \propto \frac{1}{\Delta E_{CT}(D^{+\cdot}O_2^{-\cdot})} \quad (9)$$

The authors have tried to explain this conversion of the reaction modes on the basis of the intermolecular configuration interaction (ICI) scheme.[34] It was pointed out that the HOMO–LUMO interaction by the CT_1 is essential for the (4+2) reaction, whereas the HOMO–LUMO interaction by CT_1 and LUMO–LUMO interaction by the back CT from CT_1 are crucial for the (2+2) reactions of donor-$^1O_2$ pairs (Scheme 1).[2,38,42] The CT energy levels have been successfully used to characterize the ZW mechanism for the symmetry-forbidden (2+2) type reactions between $^1O_2$ and electron-rich heterocycles, such as pyrroles. The CT character of the exciplex is semiempirically estimated by using the CT excitation energies[34] and the relationship in Fig. 7. The exciplex is converted to the zwitterion at a shorter intermolecular distance, as illustrated in Fig. 3 and Fig. 2 of Ref. 43.

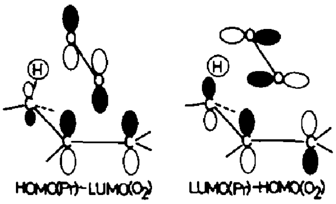
Discussions and concluding remarks

Previously, three different oxygen-approach models (A, B and C) have been considered for the ene reaction between $^1O_2$ and olefins as illustrated in Fig. 2 of Ref. 44. It was found that path B is the most favourable in the case of the propene plus $^1O_2$ system because of the predominant CT interaction. This result indicates the



Scheme 8.

importance of simultaneous attack of $^1O_2$ on the C_α–C_β double bond and allylic hydrogen at the initial stage of the ene reaction. The orbital interaction between $^1O_2$ and propene in path B is illustrated below.[9] Since the ene reaction is endothermic by *ca* 45 kcal/mol, an early (reactant-like) transition state (TS) is passed, as the reaction proceeds along the reaction co-ordinate. Therefore, the approach model B considered in our perturbation calculation should be regarded as a plausible model for the TS of ene reactions of simple olefins.[9,44] A small primary isotope effect[6,45] for the allylic hydrogen is also more compatible with the model (B) TS rather than the simplest concerted TS model A proposed by Foote and Denny.[46] Since in the CT_1 the HOMO–LUMO interaction is the main factor controlling the stabilization of the TS, the perturbation calculation predicts that the ene reaction rate of olefins of similar molecular structure should correlate with the CT_1 energy level, namely the ionization potential of a donor olefin. The intermolecular CI (ICI) result given in Table 2[9] indicates that a model system has *ca* 10% CT_1 character at the intermolecular distance $R = 2.5$ Å.



Asford and Ogryzlo,[47] and Gollnick *et al.*[48] have demonstrated that the activation energies (and rate constant) of $^1O_2$ ene reactions observed by them correlate well with the ionization potentials of the olefins.

A concerted mechanism is consistent with much of the available experimental results for the ene reactions of simple olefins,[6] and the model B-like TS[9,10] is similar to the TS models proposed by Frimer *et al.*[26] and Gollnick *et al.*[48] on experimental grounds. Many arguments[26,49] in favour of the perepoxide model are applicable to the model B-like concerted TS but not to the model A-like concerted TS.[46]

Recent laser-flash photolysis experiments for $^1O_2$ reactions by Rogers,[40] Gorman *et al.*[50] and Hurst and Schuster[51] have clearly demonstrated the important roles of charge-transfer interactions and exciplex formations at a first stage of the reactions. These experiments have revealed that an entropy-controlled process determines the relative rate of ene reactions of geomerical isomers[51] (so-called '*cis*' effect).[45] As illustrated by the orbital interactions, the model (B) TS requires the axial conformation of the allylic hydrogen, which is not the most stable conformation for a reactant olefin itself, as shown by Houk *et al.*[52] On the other hand, such a rigid gèometry is not necessary for the exciplex (π-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.[22,53–56] Therefore, there should appear an energy barrier caused by the loss of rotational freedom of alkyl groups, which is an origin of the negative entropy, along the reaction path from the exciplex to the model (B) TS, in agreement with the isotope experiments by Grdina *et al.*[45] and rotational energy barriers calculated by Houk *et al.*[52] We have proposed the two-stage concerted (TSC) mechanism[44] for ene reactions to distinguish between the two stages, namely, the model (B) TS and exciplex formations, which are rate-determining steps in cases a ($\Delta\Delta G^{\neq} > 0$) and b ($\Delta\Delta G^{\neq} < 0$),[51] respectively, as illustrated in Fig. 8. The TSC mechanism is compatible with both spectroscopic results[40,50,51] and well-established results by chemical means.[1–7] Similarly, the TSC mechanism is also conceivable for the (2+2) reactions of group III and and IV$_a$ olefins, as illustrated in Fig. 8.

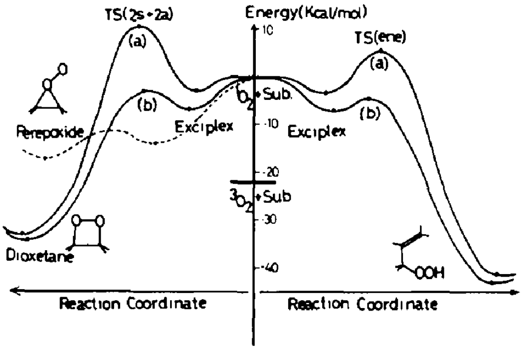
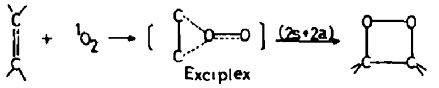


Fig. 8. Potential energy curves for (2s+2a)-like approach between $^1O_2$ and donor olefins and for ene reactions between $^1O_2$ and allylic olefins. TS indicates the transition state. Case b indicates that the exciplex formation stage is rate-determining (see text). The exciplex is largely stabilized in protic solvent or by interaction with trapping reagents. The exciplex may be converted to the perepoxide in the case of adamantylideneadamantane as illustrated by the dotted line.



The exciplex (π-complex) could be largely stabilized as a perepoxide-like intermediate (σ-complex) in the case of electron-rich hindered olefins, such as adamantylideneadamantane. Such a long-lived intermediate may be trapped bý appropriate trapping reagents, as shown by Schaap *et al.*[57]

Computational aspects

The electronic state of a composite system ($SubO_2$) is approximated by

$$\Phi_t = \Phi_r + \sum C_{rs}\Phi_s \qquad (10)$$

where Φ_t is the total wave-function of the Sub plus O_2 system, and Φ_s are various intra- and inter-molecular excited electronic configurations. The expansion coefficients C_{rs} are determined by the perturbation and configuration interaction (CI) calculations. These are defined with the properties of the wave-functions. The Coulomb energy (E_Q) is obtained from the zeroth wave-function Φ_r (Eq 10), without electron exchange between two molecules, and the exchange energy (E_X), with electron exchange between them. The wavefunction Φ_s in Eq 10 includes the three types of electronic excitations: (1) the intermolecular excitations of one molecule; (2) simultaneous excitations of both molecules; and (3) intermolecular electronic excitations between two molecules. We may define the corresponding energies for these types as: (1) the induction (E_I); (2) the dispersion (E_D); and (3) the charge-transfer (E_{CT}) energies, respectively. These energies were calculated for each reaction-path model in Figs 1 and 5 as described previously.[22] These are summarized in Table 1. When the intermolecular interactions become moderately strong, the coefficients C_{rs} are determined variationally by using the CI technique.[22] These are given in Table 2.

Acknowledgements—One of us (K.Y.) thanks Professors K. N. Houk and H. Tomioka for helpful discussions concerned with the negative activation energies observed for singlet oxygen and carbene additions to olefins.

REFERENCES

[1] M. Koizumi, S. Kato, N. Mataga and T. Matsuura, *Photosensitized Reactions*, Chaps 8 and 12. Kagakudozin, Tokyo (1977).
[2] H. H. Wasserman and R. W. Murray (Eds), *Singlet Oxygen*. Academic Press, New York (1979).
[3] M. A. J. Rogers and E. L. Powers (Eds), *Oxygen and Oxy-Radicals in Chemistry and Biology*. Academic Press, New York (1981).
[4] K. Gollnick, *Adv. Photochem.* **6**, 1 (1968).
[5] D. R. Kearns, *Chem. Rev.* **71**, 395 (1971).
[6] A. A. Frimer, *Ibid.* **79**, 359 (1979).
[7] M. Balci, *Ibid.* **81**, 91 (1981).
[8] B. H. Brandow, *Adv. Quantum Chem.* **10**, 187 (1977).
[9] K. Yamaguchi, *Chem. Rev. Jpn.* (in Japanese). **1**, 292 (1973).
[10] K. Yamaguchi, T. Fueno and H. Fukutome, *Chem. Phys. Lett.* **22**, 466 (1973).
[11] I. Saito, S. Matsugo and T. Matsuura, *J. Am. Chem. Soc.* **101**, 7332 (1979).
[12] C. S. Foote and J.-P. Lin, *Tetrahedron Lett.* 3267 (1968).
[13] M. Nakagawa, H. Okajima and T. Hino, *J. Am. Chem. Soc.* **99**, 4424 (1977).
[14] W. Ando, K. Watanabe, J. Suzuki and T. Migita, *Ibid.* **96**, 6766 (1974).
[15] A. G. Schultz and R. H. Schlessinger, *Tetrahedron Lett.* 2731 (1970).
[16] I. Saito and T. Matsuura, *Chem. Lett.* 1169 (1972).
[17] P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.* **92**, 3223 (1970).
[18] S. Mazur and C. S. Foote, *Ibid.* **92**, 3225 (1970).
[19] C. W. Jefford and C. G. Rimbault, *Ibid.* **100**, 6437 (1978).
[20] R. S. Mulliken and W. B. Pearson, *Molecular Complexes*. Wiley, New York (1969).
[21] J. N. Murrell, M. Randić and D. R. Williams, *Proc. Roy. Soc. A* **284**, 566 (1965).
[22] T. Fueno, S. Nagase, K. Tatsumi and K. Yamaguchi, *Theoret. Chim. Acta Berlin* **26**, 43 (1972).
[23] K. Yamaguchi, T. Fueno, I. Saito and T. Matsuura, *Tetrahedron Lett.* 4087 (1980).
[24] K. Yamaguchi, T. Fueno, I. Saito and T. Matsuura, *Ibid.* 3433 (1979).
[25] P. D. Bartlett and A. A. Frimer, *Heterocycles* **11**, 419 (1978).
[26] A. A. Frimer, P. D. Bartlett, A. F. Boschung and J. G. Jewett, *J. Am. Chem. Soc.* **99**, 7977 (1977).
[27] N. M. Hasty and D. R. Kearns, *Ibid.* **95**, 3380 (1973).
[28] C. W. Jefford and A. F. Boschung, *Tetrahedron Lett.* 4771 (1976).
[29] J. H. MaCapra and I. Beheshti, *J. Chem. Soc. Chem. Commun.* 517 (1977).
[30] N. J. Turro, W.-F. Chow and Y. Ito, *J. Am. Chem. Soc.* **100**, 5580 (1978).
[31] J. H. Wieringa, J. Strating, H. Wynberg and W. Adam, *Tetrahedron Lett.* 169 (1972).
[32] N. J. Turro, V. Ramamurthy, K.-C. Liu, A. Krebs and R. Kemper, *J. Am. Chem. Soc.* **98**, 6758 (1976).
[33] E. W. Meijer and H. Wynberg, *Tetrahedron Lett.* 785 (1981).
[34] K. Yamaguchi, Ph.D. Thesis (1972), and Annual Meeting of Japanese Chemical Society, March (1972).
[35] K. Yamaguchi, in *Singlet Oxygen* (Edited by A. A. Frimer), Vol. 3. CRC Press, Boca Raton, Florida (1984).
[36] M. J. Thomas and C. S. Foote, *Photochem. Photobiol.* **27**, 683 (1978).
[37] I. Saito, T. Matsuura and K. Inoue, *J. Am. Chem. Soc.* **105**, 3200 (1983).
[38] D. Rehm and A. Weller, *Ber. Bunsenges. Physik. Chem.* **73**, 834 (1969).
[39] I. Saito, T. Matsuura and K. Inoue, *J. Am. Chem. Soc.* **103**, 188 (1981).
[40] G. Peters and M. A. J. Rogers, in *Oxygen and Oxy-Radical in Chemistry and Biology* (Edited by M. A. J. Rogers and E. J. Peters). Academic Press, New York (1981).
[41] N. D. Epiotis, *J. Am. Chem. Soc.* **95**, 1925 (1972).
[42] K. Yamaguchi, T. Fueno and H. Fukutome, *Chem. Phys. Lett.* **22**, 461 (1973).
[43] K. Yamaguchi, S. Yabushita and T. Fueno, *Ibid.* **78**, 566 (1981).
[44] K. Yamaguchi, in *Oxygen and Oxy-Radicals in Chemistry and Biology* (Edited by M. A. J. Rogers and E. L. Powers), p. 409. Academic Press, New York (1981).
[45] M. Grdina, M. Orfanopoulos and L. M. Stephenson, *J. Am. Chem. Soc.* **101**, 3111 (1979).
[46] C. S. Foote and R. W. Denny, *Ibid.* **93**, 5162 (1971).
[47] R. D. Asford and E. A. Ogryzlo, *Ibid.* **97**, 3604 (1975).
[48] K. Gollnick, H. Hartmann and H. Paur, in *Oxygen and Oxy-Radicals in Chemistry and Biology* (Edited by M. A. J. Rogers and E. L. Powers), p. 379. Academic Press, New York (1981).
[49] K. R. Kopecky and H. J. Reich, *Can. J. Chem.* **43**, 2265 (1965).
[50] A. A. Gormann, I. R. Gould and T. Hamblett, *J. Am. Chem. Soc.* **104**, 7098 (1982).
[51] J. R. Hurst and G. B. Schuster, *Ibid.* **104**, 6854 (1982).
[52] K. N. Houk, J. C. Williams Jr., P. A. Mitchell and K. Yamaguchi, *Ibid.* **103**, 949 (1981).
[53] J. J. Zupancic and G. B. Schuster, *Ibid.* **103**, 944 (1981).
[54] N. J. Turro, G. F. Lehr and J. A. Butcher Jr., *Ibid.* **104**, 1754 (1982).
[55] B. Giese, W.-B. Lee and C. Neumann, *Angew. Chem. Int. Ed. Engl.* **21**, 310 (1982).
[56] H. Tomioka, N. Hayashi, Y. Izawa and M. T. H. Liu, *J. Am. Chem. Soc.* **106**, 454 (1984).
[57] A. P. Schaap, S. G. Recher, G. R. Faller and S. R. Villasenor, *Ibid.* **105**, 1961 (1983).