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MECHANISTIC CONSIDERATIONS ON PHOTOREACTION OF ORGANIC COMPOUNDS VIA EXCITATION OF CONTACT CHARGE TRANSFER COMPLEXES WITH OXYGEN

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Abstract—Reactions of various organic compounds induced by excitation of their contact charge transfer (CCT) pairs with oxygen were classified into three types of behaviour on the basis of reaction products. It is proposed that the excited state of the CCT pairs gives the products through the most isoenergetic course along the plausible exothermic pathway.

It has been recognized that several colourless compounds, such as freshly distilled N,N-dimethylaniline, become slightly coloured on contact with air and the colour fades reversibly on subsequent deaeration. In the absorption spectrum these compounds exhibit, under air, new absorption bands in longer wavelength regions than their original absorption ends. These phenomena have been attributed to the formation of contact charge transfer (CCT) pairs between the organic compounds and molecular oxygen.[1]

Many organic compounds are oxygenated on irradiation, either through generation of free radicals derived from the substrates or sensitizers employed[2a,c] or by singlet oxygen generated by dye sensitization.[2b,3] However, photo-oxidation of ethers,[4] amines,[5] and other electron rich compounds[6] has been proposed to take place through excitation of their CCT pairs with oxygen. In some cases, such as N,N-dimethylaniline (DMA), no discrete products have been detected within a short irradiation time, though short lived radical cations of the substrate are formed as observed by flash spectroscopy in polar solvents, such as acetonitrile and N,N-dimethylformamide.[7]

Recently, in this laboratory, photochemistry of the CCT pairs between several types of organic compounds and oxygen has been investigated and various types of behaviour were observed depending on the structure of the substrates.[8] In this article, an attempt is made to classify various results of the photochemistry of the CCT pairs and to elucidate the mechanism controlling their behaviour.

The results of excitation of some CCT pairs between organic compounds and oxygen are summarized in Table 1 which indicates that the apparently diverse results can be classified into the following types of behaviour: (1) reactions through radical cations or neutral free radicals derived thereof; (2) reactions through singlet oxygen; and (3) collapse to the starting materials.

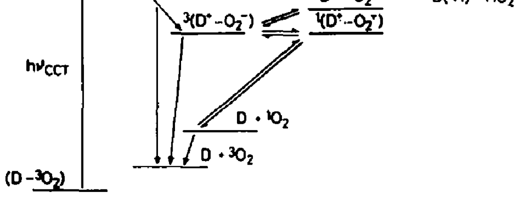
The possible roles of the excited CCT pairs in photo-oxidation can be depicted in Scheme 1.[9] On irradiation, the ground state (triplet) CCT pair gives a triplet charge transfer state.

The triplet excited CCT pair could be converted to the triplet excited substrate and singlet oxygen as well as to the triplet substrate and ground state oxygen when these processes are accompanied by lowering of the Gibbs' function. The latter process can be followed by formation of singlet oxygen and the ground state substrate if the triplet substrate has sufficient energy to excite oxygen. When the substrate is reactive with singlet oxygen, it will be oxygenated with the singlet oxygen generated; however, when it is not reactive, the resulting singlet oxygen is deactivated to the ground state and, thus, dissipation of the excitation energy is accomplished.

Alternatively, the excited CCT pair could give rise to the substrate cation radical pair and the superoxide ion, particularly in polar solvents. The energy of the radical ion pair can be approximately estimated by $E(D^{+\cdot}/D) - E(O_2/O_2^{-\cdot})$. The radical ion pair, initially formed in the triplet state, could undergo intersystem crossing to the singlet pair which, subsequently, undergoes back electron transfer to give singlet oxygen and the substrate in the ground state if the conditions are suitable.

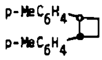
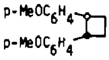
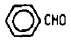
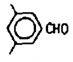
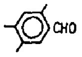
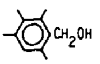
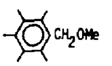
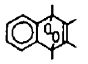
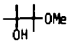
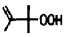
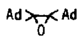
However, when the triplet CCT pairs lie in sufficiently low energy to be close to the ground state, particularly as is the case for those of substrates with low oxidation potentials, the triplet pairs will be easily deactivated to the ground state, and, thus, this process will also work as a deactivation process.

As described below, the apparently diverse behaviour of the CCT pairs can be understood in terms of classified types of reaction courses. Furthermore, as to what factors govern the reaction courses of the



Scheme 1. Reaction process of excited CCT pairs.

Table 1. Reaction products on CCT complex excitation and some properties of donor molecules

Compound	Product	Type of reaction[a]	Interaction with $^1O_2$[b]	Ionization energy (eV)	Oxidation potential (V vs SCE)	CCT pair absorption end (eV)
Styrenes						
p-Methyl-		$D^{+\cdot}$	—	—	1.72[l]	> 3.35
p-Methoxy-		$D^{+\cdot}$	—	—	1.49[j]	< 3.10
Polymethylbenzenes						
Toluene		$D^{+\cdot c}$	—	8.81[h]	2.27	—
1,3,5-Trimethyl-		$D^{+\cdot}$	—	8.39[h]	2.11	—
1,2,4,5-Tetramethyl-		$D^{+\cdot}$	—	8.03[h]	1.83	—
Pentamethyl-		$D^{+\cdot}$	—	7.92[h]	1.71	—
Hexamethyl-		$D^{+\cdot}$	1,4-add[d]	7.85[h]	1.69	3.18
Naphthalenes						
2,3-Dimethyl-		$^1O_2$	1,4-add[d]	7.85[h]	1.51[l]	< 2.95
1,2,3,4-Tetramethyl-		$^1O_2$	1,4-add	—	1.55	< 2.95
Anisoles						
p-Methyl-		NR	—	8.18[i]	1.69	2.95
p-Methoxy-		NR	—	—	1.59	2.95
Anilines						
N,N-Dimethyl-		NR	quench[e]	7.37[i]	0.79[m]	< 2.48
N,N-Dimethyl-*p*-methyl-		NR	quench[e]	7.27[i]	0.75[m]	2.14
DABCO		NR	quench[e]	7.23[j]	0.69[m]	3.54
Polysubstituted olefins						
2,3-Dimethyl-2-butene		$D^{+\cdot}$	ene[f]	8.30[f]	1.59	3.02
		$^1O_2$				
Adamantylideneadamantane		$D^{+\cdot}$	1,2-add[g]	7.84[k]	1.45	—

[a] $D^{+\cdot}$, Reaction through radical cations or free radicals derived thereof; $^1O_2$, reaction through singlet oxygen; NR, no reaction.

[b] 1,2-add, 1,2-Cycloaddition; 1,4-add, 1,4-cycloaddition; ene, ene reaction quench, quenching.

[c] Ref. 22.

[d] Ref. 14*a*.

[e] Ref. 29.

[f] Ref. 26.

[g] Ref. 33.

[h] J. B. Birks, *Photophysics of Aromatic Molecules*, p. 470. Wiley, New York (1970).

[i] Ref. 19.

[j] L. L. Miller, G. D. Nordblon and E. A. Mayeda, *J. Org. Chem.* **37**, 916 (1972).

[k] P. D. Mollere, K. N. Houk, D. S. Bomse and T. H. Morton, *J. Am. Chem. Soc.* **98**, 4732 (1976).

[l] The value is estimated from E_{ox} vs a $Ag/AgNO_3$ electrode by adding 0.27 V [J. N. Butler, in *Advances in Electrochemistry and Electrochemical Engineering* (Edited by P. Delahay and C. W. Tobias), Vol. 7. Interscience, New York (1970)].

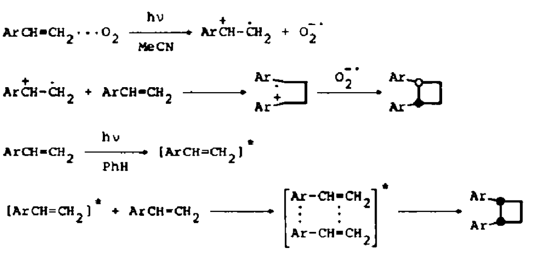
[m] Tetraethylammonium perchlorate was used as a supporting electrolyte.

excited CCT pairs, we should like to propose that the excited CCT pairs prefer the most isoenergetic path giving the products among the exothermic processes.

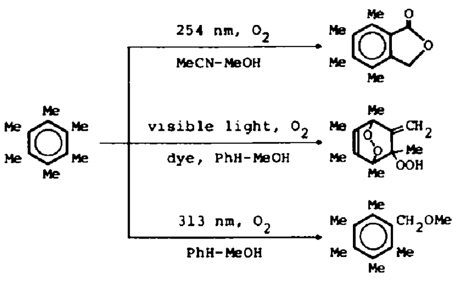
RESULTS AND DISCUSSION

Styrenes

Selective excitation of the CCT pair of 4-methoxystyrene (MeOSt) with oxygen with 366 nm light in acetonitrile under oxygen gave *trans*-1,2-di(4-methoxyphenyl)cyclobutane as the main product.[8b] The formation of the *trans*-isomer can be ascribed to the reaction of MeOSt radical cations. The excitation of the CCT pairs leads to electron transfer from MeOSt to oxygen to afford MeOSt radical cations and the superoxide ions. The former radicals add to MeOSt to give radical cations of the dimer in which both aromatic groups are apart from each other to avoid steric



Scheme 2.



Scheme 3.

crowding. These radical cations accept an electron from the superoxide ions and cyclize to afford the above product. However, excitation of the CCT pairs in benzene did not give any product.[8b] This is probably due to ineffective charge separation in the CCT pairs in the non-polar solvent. In contrast to the CCT pair excitation, direct excitation of MeOSt with shorter wavelength light (313 nm) under nitrogen afforded *cis*-1,2-di(4-methoxyphenyl)cyclobutane. This must be through the formation of an excimer of MeOSt; in the excimer the π-electron systems of each component molecules would interact at both the ethylenic linkage and the aromatic ring.[8b]

The result that 4-methylstyrene afforded dimers, a cyclobutane and a cyclohexane on CCT excitation can be understood on the same basis.[8b]

Formation of triplet MeOSt (T_T estimated as 2.7 eV)† from the excited CCT pair of MeOSt (nearly 3.10 eV as estimated from the CCT absorption end) must be possible. However, planar triplets ($^3t^*$) of olefins undergo twisting quickly to perpendicular triplets ($^3p^*$).[11] Since, generally, $^3p^*$ lies very close in energy to the perpendicular ground state (p^0),[11] $^3p^*$ cannot undergo energy transfer to oxygen but quickly undergoes crossing to p^0 enhanced by the presence of oxygen. Even if singlet oxygen is generated, MeOSt is less reactive with it.[12] Consequently, the triplet formation serves to dissipate the energy of the excited CCT pair and the alternative path giving the radical ion pair (2.36 eV)‡ will predominate to result in reaction products.

Polymethylbenzenes

Behaviour of polymethylbenzene varies with the number of methyl groups and nature of other substituents.[8a] Hexamethylbenzene (HMB) undergoes various types of reactions depending upon conditions of excitation.[8a,14] Direct excitation with 254 nm light led to oxidation of the methyl groups[8a] and irradiation with visible light in the presence of dye sensitizers, such as methylene blue, resulted in 1,4-cycloaddition of singlet oxygen followed by ene-reaction of the resulting endo-peroxide with singlet oxygen to give a hydroperoxy endo-peroxide.[8a,14a] On the other hand, selective excitation of the CCT pairs with 313 nm light in a solution containing methanol afforded a product resulting from methanolysis of pentamethylbenzyl cations[8a] which might arise from deprotonation of HMB radical cations followed by further one-electron oxidation. This result provides a reasonable understanding of the formation of the above methanolysis product reported on irradiation of HMB with a sun lamp in the presence of methylene blue.[14b]

In the radical ion pairs of a HMB radical cation and a superoxide ion, the former will be easily deprotonated to give a pentamethylbenzyl radical and a hydroperoxy radical. This process is reasonable since pK_a values of polymethylbenzene cation radicals are estimated as highly negative[15] and that of the hydroperoxy radical, the conjugated acid of the superoxide ion,[16] is reported to be 4.4–4.8.[17] The resulting pentamethylbenzyl radicals could be further oxidized through electron transfer by HMB radical cations to afford pentamethylbenzyl cations which react finally with methanol to give methoxymethylpentamethylbenzene. An alternative pathway for the formation of pentamethylbenzyl cations might be a sequential electron–proton–electron transfer in the radical ion pairs. Thus, pentamethylbenzyl radicals formed could be further oxidized by hydroperoxy radicals to give pentamethylbenzyl cations and hydroperoxide anions. The oxidation potential of unsubstituted benzyl radicals can be estimated to be very close to that of N,N-dimethylaniline (DMA), 0.97 V,[18] since the ionization energies of benzyl radicals and DMA are nearly the same, i.e. 7.20[18] and 7.37 eV,[19] respectively. Introduction of many methyl groups to benzyl radicals will lower the oxidation potentials of the radicals. In view of the fact that HMB (E_{ox} 1.69 V) shows an oxidation potential nearly 0.6 V lower than that of toluene (E_{ox} 2.27 V), the oxidation potential of pentamethylbenzyl radicals must be nearly 0.4 V. Furthermore, since the electron affinity of hydroperoxy radicals is reported to be considerably large[20] and this process gives the highly reactive species, it could be possible kinetically, although slightly endothermic.

Reactions of triarylmethanes to give products through triarylmethyl cations belong to the same type of reaction.[21]

Several compounds afford products arising from neutral free radicals which must be produced from the corresponding radical cations or cationoids. Photooxygenation, through excitation of the CCT pairs of some polymethylbenzenes,[8a,22] diethyl ether,[4] and triethylamine[5,22] with oxygen, belongs to this category.

Excitation of the CCT pairs of 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene with oxygen, in a mixture of benzene and methanol, gave 3,5-dimethylbenzaldehyde and 2,4,5-trimethylbenzaldehyde together with the corresponding acid, respectively; however, in these cases any trace amounts of methoxymethylpolymethylbenzenes, such as 1-methoxymethyl-3,5-dimethylbenzene and 1-methoxy-

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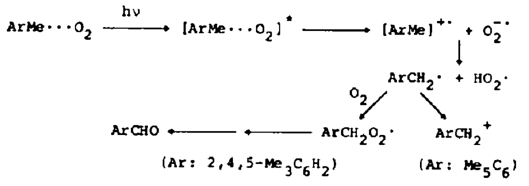
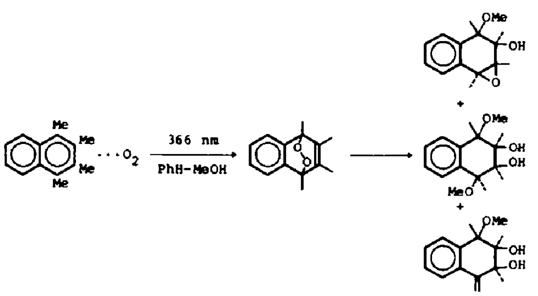
† Triplet excitation energy of styrene, 61.7 kcal/mol.[10]

‡ Estimated as $E(D^{+\cdot}/D) - E(O_2/O_2^{-\cdot})$ where $E(D^{+\cdot}/D) = 1.49$ V and $E(O_2/O_2^{-\cdot}) = -0.87$ V vs SCE.[13]



Scheme 4.



Scheme 5.

methyl-2,4,5-trimethylbenzene, were not afforded[8e] in contrast to the excitation of the CCT pairs of HMB with oxygen. These results are related to the report that 9,10-dicyanoanthracene-sensitized oxygenation of mono- to tetramethylbenzenes in acetonitrile gives the corresponding aldehydes and acids, probably through substrate radical cations and the corresponding benzyl radicals.[23]

Methoxy-substituted methylbenzenes, such as 4-methoxytoluene and 1-methoxy-3,5-dimethylbenzene, gave neither methoxylated nor oxygenated products on excitation of their CCT pairs in methanol–benzene despite having oxidation potentials comparable to, or slightly lower than, that of HMB.[24]

These results indicate that, among arylmethyl radicals, pentamethylbenzyl radicals[8a] are readily oxidized to their corresponding carbocations in preference to being oxygenated; however, other arylmethyl radicals are resistant to the one-electron oxidation and easily react with oxygen to give oxygenation products. The mechanism is depicted in Scheme 4.

As to inertness of 4-methoxytoluene and 1-methoxy-2,3-dimethylbenzene,[24] they are expected to give radical cations on excitation of their CCT pairs because of their low oxidation potentials. However, it is reasonable to suppose that in these radical cations electron donation from the methoxy group reduces their acidity compared with toluene radical cations which are not deprotonated to give neutral benzyl radicals.

1,2,3,4-*Tetramethylnaphthalene*

Excitation of the CCT pairs of 1,2,3,4-tetramethylnaphthalene (TMN) with oxygen in various solvents with 366 nm light afforded the 1,4-endo-peroxide of TMN and its derivatives; however, methanolysis products resulting from HMB were not formed in solutions containing methanol.[8c] The formation of the endo-peroxide is attributed to the reaction of TMN with the singlet oxygen generated.[25] Even in the presence of 2,3-dimethyl-2-butene (DMB), 366 nm light can selectively excite the CCT pairs of TMN with oxygen in acetonitrile to afford a mixture of a hydroperoxide of DMB[26] and the endo-peroxide of TMN in the same ratio as in erythrosine-sensitized oxygenation of the same mixture of DMB and TMN in acetonitrile.[8c]

That TMN gives the products corresponding with reaction with singlet oxygen but none corresponding with reaction with benzyl-type radicals or cations, in spite of its oxidation potential being lower than HMB, means that the excited CCT pair of TMN prefers singlet oxygen production to radical cation production in contrast to HMB which gives exclusively the product arising from the radical ions. Formation of triplet TMN and singlet oxygen (3.43 eV)† from the excited CCT pairs of TMN with oxygen (nearly 2.95 eV) is an endothermic process. However, formation of triplet TMN and ground state oxygen (2.46 eV) is an exothermic process; triplet TMN affords singlet oxygen.

Alternatively, the excited CCT pairs of TMN with oxygen could give radical ion pairs of TMN$^{+\cdot}$ and $O_2^{-\cdot}$ (2.42 eV) in an energetically favourable process and the resulting ion pairs would give singlet oxygen and TMN. However, if the radical cations were efficiently produced from the TMN–O_2 pairs, they would give, as in the case of HMB–O_2 pairs, the corresponding arylmethyl cations, which would be methanolysed.

Therefore, it is reasonable to propose that the excited TMN–O_2 pairs take a more isoenergetic process to give triplet TMN followed by energy transfer to oxygen so generating singlet oxygen in preference to the formation of the radical ion pairs. On the other hand, the excited HMB–O_2 pairs (3.18 eV) cannot undertake an endothermic process giving triplet HMB (3.40 eV)‡ but lead to the production of the radical ion pairs (2.56 eV). For MeOSt, as discussed above, the most isoenergetic process leading to its triplet does not result in chemical reactions, but the alternative process affording the radical ions predominates to give the products.

Furthermore, that no products ascribable to singlet oxygen were afforded from the HMB–O_2 pairs indicates that HMB$^{+\cdot}$–$O_2^{-\cdot}$ pairs do not efficiently give singlet oxygen. The fact that singlet oxygen formation from these radical ion pairs is an exothermic process seems to be reflected in the isoenergetic condition between the radical ion pairs and singlet oxygen being important in accomplishing electron transfer. It is noticeable that the electron transfers hitherto confirmed between radical cations and the superoxide ion are in the couples containing the radical cations of electron donors with relatively low oxidation potentials, such as ferrocene (E_{ox} 0.3 V),[27] 1,3-diphenylisobenzofuran (E_{ox} 0.8 V)[27] and thianthrene (E_{ox} 1.25 V).[28]

Amino compounds

Many compounds exhibiting the CCT absorption do not result in any products on irradiation and are recovered unchanged, although the substrates might be

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† The triplet excitation energy of TMN was determined to be 56.7 kcal/mol from its phosphorescence spectrum.[24]

‡ Triplet excitation energy of HMB: 78.4 kcal/mol.[10]

consumed on prolonged irradiaton. For example, N,N-dimethylaniline (DMA),[5] N,N-dimethyl-4-methylaniline[5] and DABCO are not effectively oxygenated on CCT excitation. Most compounds which are unreactive or nearly unreactive on CCT excitation are either quenchers of singlet oxygen or unreactive towards singlet oxygen.[29]

The CCT pairs of DMA and DABCO with oxygen are expected to afford easily the corresponding radical cations and superoxide ions because of their low oxidation potentials (0.79 and 0.69 eV for DMA and DABCO, respectively) and to dissociate into the component radical ions in polar solvents. In these cases, the radical ion pairs (1.66 and 1.56 eV for DMA and DABCO, respectively) as well as the triplet charge transfer state are close in energy to the ground state and, accordingly, the pairs will be easily deactivated to the ground state.

The situation of the radical ion pairs being nearly isoenergetic with singlet oxygen (0.97 eV) would facilitate the reversible conversion between the radical ion pairs and singlet oxygen. Since it is reported that quenching of singlet oxygen generated thermally from a water-soluble endo-peroxide by 4-methoxy-N,N-dimethylaniline (E_{ox} 0.5 V) in water gives the superoxide ion,[30] the quenching of singlet oxygen with efficient quenchers would result in electron transfer to give pairs of the radical cation of the quencher and the superoxide ion; the quencher radical cations would undergo facile collapse to the starting materials or undergo oxidative cleavage on prolonged irradiation.

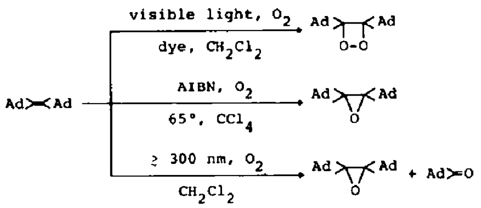
In relation to the reactions of amines, sulphides are reported to form the CCT pairs with oxygen and to give sulphoxides on their excitation. Taking into account their low oxidation potentials, the initial process can be assumed to be electron transfer from the sulphides to oxygen.[31]

Polysubstituted olefins

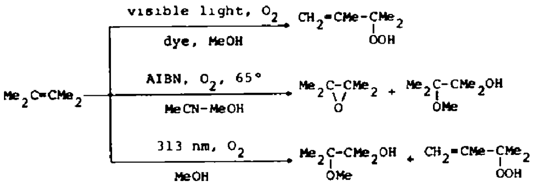
The results of excitation of the CCT pairs of polysubstituted olefins, such as adamantylideneadamantane (ADA)[8f] and 2,3-dimethyl-2-butene (DMB)[8g] are more complicated, since their AIBN-initiated autoxidation, dye-sensitized oxygenation and 9,10-dicyanoanthracene(DCA)-sensitized oxygenation afford some of the same products which are obtained from their CCT pair excitation.

Irradiation of ADA under oxygen in dichloromethane through a Pyrex wall afforded its epoxide and adamantanone. On the other hand, the AIBN-initiated autoxidation gave the epoxide exclusively and methylene blue-sensitized oxygenation with visible light in dichloromethane afforded exclusively the dioxetane of ADA.[32] Moreover, DCA-sensitized oxygenation gives the dioxetane.[33] ADA radical cations generated from anodic oxidation of ADA are known to react with oxygen to give the corresponding peroxy radical cations which, subsequently, accept an electron from ADA to give the dioxetane.[34]

Irradiation of the CCT pairs of DMB in the presence of methanol led to the formation of 3-methoxy-2,3-dimethyl-2-butanol and 3-hydroperoxy-2,3-dimethyl-1-butene.[8g] The dye-sensitized oxygenation of DMB is well known to afford the hydroperoxide,[26] and the AIBN-initiated autoxidation gave the corresponding epoxide and the methoxybutanol in the presence of methanol.[8g]



Scheme 6.



Scheme 7.

Addition of DABCO to the CCT pairs of DMB under irradiation reduced the formation of all the products. However, the effect of DABCO cannot differentiate whether or not singlet oxygen participates, since DABCO retards both of the singlet oxygen and free radical reactions.[35]

Production of triplet DMB (estimated as *ca* 3.39 eV)† from the excited CCT pairs of DMB (3.0 eV) is not probable, but the formation of the radical ion pairs (2.39 eV) is probable.

It is worth mentioning that, on measurement of cyclic voltammetry (CV), oxygen in the atmosphere reduces the electric current at the oxidation potential of DMB to nearly half the value compared to that observed in the absence of oxygen in acetonitrile with tetrabutylammonium perchlorate, whereas the current of CV oxidation of stilbene is not affected by oxygen. This result means that on the anode one electron oxidation of DMB to its radical cations is rapidly followed by its facile deprotonation to give allylic radicals and by their further one electron oxidation in the absence of oxygen; however, oxygen intercepts the intermediate species which in its absence would discharge at the electrode surface. In contrast, on CV oxidation of stilbene the resulting radical cations are reluctant to be deprotonated and, thus, suffer no oxygen effect.

Therefore, it is probable that the radical cations arising from the excitation of the CCT pairs give the products without participation of singlet oxygen.

CONCLUSION

As discussed above, the excitation of the CCT pairs of various organic compounds with oxygen leads to apparently versatile reactions which can be classified into three categories. The reaction courses depend upon behaviour of the excited CCT pairs which take the most isoenergetic process resulting in chemical reactions along the plausible exothermic pathway.

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† Triplet excitation energy of 2-butene: 78.2 kcal/mol.[10]

EXPERIMENTAL

Photo-oxidations. Solns of organic substrates in appropriate solvents were irradiated in an O_2 stream with 313 or 366 nm light from a 400 W or 1 kW high pressure mercury lamp. The 313 nm light was produced through an aq potassium chromate soln and that of 366 nm through either a Toshiba UV-D36B glass filter or a uranium wall. The products were isolated in the usual manner and identified by comparing their spectral data with those of authentic samples. Their yields were determined by GLPC (Shimadzu GC-4CM) or HPLC (Shimadzu LC-2).

$^1O_2$ was generated by irradiating sample solns containing methylene blue as a sensitizer under O_2 with a 650 W tungsten–bromine lamp through a Pyrex wall.

Autoxidation was carried out by employing AIBN as an initiator at 65°.

Cyclic voltammetry. Cyclic voltammetry was performed with a hand-made electrochemical cell system in the three electrode mode equipped with a Hokuto HA-201 potentiostat and a Hokuto HB-104 function generator. A Pt wire, a Pt gauze and an SCE were used as the working, counter and reference electrodes, respectively. Cyclic voltamgrams were obtained after 20 min bubbling of Ar or O_2 into acetonitrile solns containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte.

The effect of O_2 was estimated by comparing peak heights of the current–potential curves.

REFERENCES

[1a] M. Tamres and R. L. Strong, in *Molecular Association* (Edited by R. Foster), Vol. 2, p. 397. Academic Press, London (1979); [b]D. F. Evans, *J. Chem. Soc.* 345 (1953); 1351, 3885 (1957); 2753 (1959); 1735 (1960); 1987 (1961); [c]H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.* **82**, 5966 (1960).

[2a] T. Matsuura, *Sanso Sanka Hanno* (*Oxidation Reactions with Molecular Oxygen*), Chaps 6, 10. Maruzen, Tokyo (1977); [b]*Ibid.* Chap. 9; [c]M. Koizumi, S. Kato, N. Mataga, T. Matsuura and Y. Usui, *Photosensitized Reactions*, Chaps 7, 12. Kagaku Dojin, Kyoto (1978).

[3] H. H. Wasserman and R. W. Murray (Editors), *Singlet Oxygen.* Academic Press, New York (1979).

[4a] C. Von Sonntag, K. Newwald, H.-R. Schuchmann, F. Weck and E. Janssen, *J. Chem. Soc. Perkin Trans. 2* 171 (1975); [b]V. I. Steinberg, R. D. Olson, C. T. Wang and N. Kulevsky, *J. Org. Chem.* **32**, 3227 (1967).

[5] H. Tsubomura, T. Yagishita and H. Toi, *Bull. Chem. Soc. Jpn.* **46**, 3051 (1973).

[6a] N. Kulevsky, P. V. Sneeringer and V. I. Stenberg, *J. Org. Chem.* **37**, 438 (1972); [b]N. Kulevsky, P. V. Sneeringer, L. D. Grina and V. I. Stenberg, *Photochem. Photobiol.* **12**, 395 (1970); [c]V. I. Stenberg, P. V. Sneeringer, C. Niu and N. Kulevsky, *Ibid.* **16**, 81 (1972).

[7] M. Hori, H. Itoi and H. Tsubomura, *Bull. Chem. Soc. Jpn.* **43**, 3765 (1970).

[8a] K. Onodera, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.* **21**, 2831 (1980); [b]M. Kojima, H. Sakuragi and K. Tokumaru, *Ibid.* **22**, 2889 (1981); [c]H. Sakuragi, G. Furusawa, K. Ueno and K. Tokumaru, *Chem. Lett.* 1213 (1982); [d]R. Akaba, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.* **25**, 665 (1984); [e]H. Sakuragi, K. Onodera, G. Furusawa and K. Tokumaru, Presented at *14th Symposium on Oxidation Reactions*, abstracts, p. 114. Yokohama (1980); [f]R. Akaba, H. Sakuragi and K. Tokumaru, Presented at *34th Symposium on Organic Reaction Mechanisms*, abstracts, p. 88. Sapporo (1983); [g]M. Tsuchiya, G. Furusawa, H. Sakuragi and K. Tokumaru, Presented at *49th Annual Meeting of the Chemical Society of Japan*, abstracts II, p. 872. Tokyo (1984); [h]K. Tokumaru, H. Sakuragi and R. Akaba, *Kagaku* (*Chemistry*) **38**, 145 (1983).

[9a] J. B. Birks, in *Organic Molecular Photophysics* (Edited by J. B. Birks), Vol. 2, p. 545. Wiley, New York (1975); [b]R. S. Davidson and J. E. Pratt, *Tetrahedron* **40**, 999 (1984); [c]L. E. Manring, C.-I. Gu and C. S. Foote, *J. Phys. Chem.* **87**, 40 (1983).

[10] S. L. Murov, *Handbook of Photochemistry.* Marcel Dekker, New York (1973).

[11a] J. Saltiel and J. L. Charlton, *Rearrangement in Ground and Excited States* (Edited by P. de Mayo), Vol. 3, p. 25. Academic Press, New York (1980); [b]T. Arai, H. Sakuragi and K. Tokumaru, *Bull. Chem. Soc. Jpn.* **55**, 2204 (1982); [c]H. Goerner, *J. Phys. Chem.* **86**, 2028 (1982); [d]C. S. Nakagawa and P. J. Sigal, *J. Chem. Phys.* **58**, 3529 (1973); [e]R. A. Caldwell, G. W. Sovocool and R. J. Persie, *J. Am. Chem. Soc.* **95**, 1496 (1973); [f]M. G. Rockey and K. Salisbury, *J. Chem. Soc. Perkin Trans 2* 1582 (1973).

[12] G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.* 3609 (1969).

[13] D. T. Sawyer, G. Chiericato, Jr., C. T. Angelis, E. J. Nanni, Jr. and T. Tsuchiya, *Anal. Chem.* **54**, 1720 (1982).

[14a] C. J. M. Van den Heuvel, H. Steinberg and T. J. De Boer, *Recl., J. R. Netherl. Chem. Soc.* **96**, 157 (1977); [b]H. H. Wasserman, P. S. Mariano and P. M. Keehn, *J. Org. Chem.* **36**, 1765 (1971).

[15a] A. M. de P. Nicholas and D. Arnold, *Can. J. Chem.* **60**, 2165 (1982); [b]A. M. de P. Nicholas, R. J. Boyd and D. Arnold, *Ibid.* **60**, 3011 (1982); [c]M. M. Green, S. L. Mielke and T. Mukhopadhyay, *J. Org. Chem.* **49**, 1276 (1984); [d]K. Sehested and J. Holcman, *J. Phys. Chem.* **82**, 651 (1978).

[16] D. T. Sawyer and M. J. Gibian, *Tetrahedron* **35**, 1471 (1979).

[17a] G. Czapski and B. H. J. Bielski, *J. Phys. Chem.* **67**, 2180 (1963); [b]J. Rabani and S. O. Nielsen, *Ibid.* **73**, 3736 (1969).

[18] F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.* **100**, 3290 (1978).

[19] T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.* **47**, 2563 (1974).

[20a] V. M. Bierbaum, R. J. Schmitt, C. H. DePuy, R. D. Mead, P. A. Schulz and W. C. Lineberger, *J. Am. Chem. Soc.* **103**, 6262 (1981); [b]S. W. Benson and P. S. Nangia, *Ibid.* **102**, 2843 (1980).

[21] J. E. Kuder, W. W. Limburg, M. Stolka and S. R. Turner, *J. Org. Chem.* **44**, 761 (1979).

[22] K. S. Wei and A. H. Adelman, *Tetrahedron Lett.* 3297 (1969).

[23] I. Saito, K. Tamoto and T. Matsuura, *Ibid.* 2889 (1979).

[24] G. Furusawa, M S Thesis, University of Tsukuba (1982).

[25] A. P. Schaap and K. A. Zaklika, in *Singlet Oxygen* (Edited by H. H. Wasserman and R. W. Murray), Chap. 6. Academic Press, New York (1979).

[26] K. Gollnick and H. J. Kuhn, *Ibid.* Chap. 8.

[27] F. A. Mayeda and A. J. Bard, *J. Am. Chem. Soc.* **95**, 6223 (1973).

[28] W. Ando, Y. Kabe, S. Kobayashi, C. Takyu, A. Yamagishi and H. Inaba, *Ibid.* **102**, 4526 (1980).

[29] C. S. Foote, in *Singlet Oxygen* (Edited by H. H. Wasserman and R. W. Murray), Chap. 5. Academic Press, New York (1979).

[30] I. Saito, T. Matsuura and K. Inoue, *J. Am. Chem. Soc.* **103**, 188 (1981).

[31] T. Tezuka, H. Miyazaki and H. Suzuki, *Tetrahedron Lett.* 1959 (1978).

[32] J. H. Wieringa, J. Strating, H. Wynberg and W. Adam, *Ibid.* 169 (1972).

[33] W. Ando, Y. Kabe and T. Takata, *J. Am. Chem. Soc.* **104**, 7314 (1982).

[34a] S. F. Nelsen and R. Akaba, *Ibid.* **103**, 2096 (1981); [b]E. L. Clennan, W. Simmons and C. W. Almgren, *Ibid.* **103**, 2098 (1981).

[35] T. Kanno, M. Hisaoka, H. Sakuragi and K. Tokumaru, *Bull. Chem. Soc. Jpn.* **54**, 2330 (1981).