

Singlet Oxygen

Reactions with Organic Compounds and Polymers

Edited by

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Singlet Oxygen

Preface

Excited forms of molecular oxygen of high chemical activity were discovered in Germany in the 1930s and classified spectroscopically in Canada as two singlet forms. The remarkable properties of singlet oxygen in organic reactions were re-discovered in the USA in 1964. Since then, we have witnessed a rapid increase in activity in studies of singlet oxygen. Organic chemists have developed singlet oxygen as a specific oxidative reagent. Singlet oxygen has been interpreted to be an active photochemical intermediate in polluted air. More recently, efforts have been made to relate photo-oxidative reactions of polymers to singlet oxygen.

This book describes the structure and properties of singlet oxygen and its reactions with organic compounds and polymers. This material is the basis for important practical and technical considerations of the role of singlet oxygen in environmental pollution and health hazards. The chapters of the book are based on papers presented at the EUCHEM Conference on Singlet Oxygen Reactions with Polymers held at Södergarn on Lidingö, Stockholm, Sweden, on September 2–4, 1976. Several chapters describe the formation of singlet oxygen, the kinetics of physical deactivation, and the kinetics and mechanisms of chemical oxidation reactions. Approximately half of the chapters deal with singlet oxygen reactions with synthetic and natural polymers and the problems of stabilization of polymers against singlet oxygen oxidation.

It is our pleasure to thank the participants of the EUCHEM Conference for their excellent contributions and cooperation in the preparation of this volume. We also acknowledge financial support for the conference from the Swedish Government through the Department of Education and a special grant from Kjell och Märta Beijers Stiftelse.

Stockholm, March, 1977

BENGT RÅNBY AND JAN F. RABEK

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The History of Singlet Oxygen—An Introduction

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The discovery of oxygen by Scheele and Priestly independently about 200 years ago was a turning-point in the development of chemical concepts (e.g. ref. 1). Until then the theory of phlogiston (with negative weight) was accepted and used for the interpretation of oxidation of metals and burning of organic matter. The crucial role of oxygen in life processes became well established during the 1800s. Oxygen had unique properties in various reactions. Already Faraday had discovered that oxygen was paramagnetic and in this way differed from other known permanent gases. This property, based on a proposed electron structure of the diatomic oxygen molecule, was interpreted by Mulliken² in 1928 as being due to its content of two outer electrons with parallel spins. This uncoupled electron pair classified oxygen as a triplet in its lowest energy state ($^3\Sigma_g^-$). A few years later, two higher energy states of oxygen were found spectroscopically by Childe and Mecke³ (the $^1\Sigma_g^+$ in 1931) and by Herzberg⁴ (the $^1\Delta_g$ in 1934). These two forms of the oxygen molecule had an excess energy of a fraction of a chemical bond (37.5 and 22.5 kcal mol⁻¹, respectively). They were classified as spectroscopic singlets, and this classification was interpreted as being the result of their outer electron pair having antiparallel spins.

These physical discoveries of oxygen in triplet and singlet forms attracted the attention of a chemist, Dr. Hans Kautsky, a 'Docent' (Assistant Professor) at Heidelberg University in Germany. He was studying the photoluminescence of organic dyes in solution and adsorbed, e.g. chlorophyll, tryptaflavin, malachite green, and porphyrins. When illuminated, the dyes absorbed quanta and were excited to higher energy states. They could return to the original low-energy state rapidly (fluorescence) or slowly (phosphorescence) by emission of quanta. Kautsky found that the presence of oxygen could largely extinguish the fluorescence of some irradiated dyes, e.g. the red fluorescence from chlorophyll.⁵ He made the correct interpretation that the excess energy of the excited dye was transferred to oxygen molecules. The energy required for the excitation of oxygen was relatively small as even the red fluorescence from chlorophyll was sufficient. Kautsky showed further that the excited oxygen molecules (he called them 'active' oxygen) could oxidize dyes which did not react with molecular

oxygen in its normal energy state.⁶ Trypaflavine (I) and leuco-malachite green (II) were adsorbed on silica gel. Illumination excited I but not II. With oxygen present with I and II mixed under illumination, the leuco-form II was oxidized to a green colour. Kautsky concluded correctly that the excitation energy of the illuminated dye I was transferred to oxygen and produced 'metastable active oxygen molecules', possibly in the $^1\Sigma$ state, which then oxidized the dye II. In other experiments, Kautsky⁷ demonstrated that the 'active oxygen' was deactivated ('quenched') by collision with other oxygen molecules and that the lifetime of 'active oxygen' was longer (10 min or more) with decreasing oxygen pressure (from 0.4 to 0.0004 mm).

Kautsky's results were extensive and his conclusions basically correct from what is known today. However, Kautsky's views were not accepted at the time and his work remained unnoticed for about 25 years. The reason was that the excited singlet oxygen, if it existed, under practical conditions (atmospheric pressure, room temperature) was considered to be a very short-lived intermediate. Instead, the photochemical reactions were interpreted as being due to atomic oxygen and ozone and this alternative was widely accepted.⁸ There was some discussion of singlet oxygen in air pollution as a possible reactive intermediate in about 1960.⁹ The re-discovery of singlet oxygen was made in 1964 by photo-oxidation experiments by Foote and Wexler¹⁰ and Corey and Taylor.¹¹ The photoinduced addition of oxygen to double bonds with an allyl hydrogen atom was well interpreted as a singlet oxygen reaction. Since then several groups have been working on the mechanism of singlet oxygen reactions in organic synthesis.

Studies also continued on the photochemical reactions in the atmosphere. Singlet oxygen was considered as a possible intermediate in 'photochemical smog' in 1966 but the mechanism of formation was unknown.¹² Direct absorption of light quanta by oxygen molecules ('a spectroscopically forbidden transition') could occur at atmospheric pressure due to the perturbed state of 3O_2 . The evidence for 1O_2 as an intermediate was obtained by Pitts *et al.*¹³ in 1969 in studies of the conversion of NO into NO_2 both in the atmosphere and under laboratory conditions. Among the reaction mechanisms possible, the best established involve olefins, ketonic radicals and ketoperoxides, and probably also ozone with singlet oxygen ($^1\Delta_g$ or $^1\Sigma_g^+$) as critical intermediates.

Singlet oxygen reactions with polymers have been studied in the last few years.¹⁴ Such mechanisms were first proposed by Trozzolo and Winslow¹⁵ in 1968 without much experimental evidence. They studied the photo-oxidation of commercial polyethylene containing carbonyl groups as sensitizers. Exposure of polyethylene surfaces to a stream of singlet oxygen was later shown to result in the formation of hydroperoxide groups.¹⁶ More extensive evidence for singlet oxygen reactions was obtained for polydienes (*cis*- and *trans*-1,4- and -1,2-vinyl).^{17,18} It has also been proposed by Rabek and Rånby¹⁹ that singlet oxygen attacks phenyl groups in polystyrene by a ring-opening reaction, giving dialdehyde side-groups containing two conjugated double bonds. Of particular interest are the initiation reactions with singlet oxygen, formed by energy

transfer from excited trace amounts of impurities in polymer samples. Such sensitizers may be deposited materials from polluted air or water or extraneous groups from the production or processing of the polymeric material.²⁰

There have been recent attempts to use singlet oxygen from a chemical process or a physical generator as a reagent for specific oxidation of chemical compounds, as a bleaching agent for paper and textile fibres and for surface treatment of plastics and rubber.²¹

REFERENCES

1. J. R. Partington, *A History of Chemistry*, Vol. 1, 1970, Vols. 2-4, Macmillan, London, 1961-64.
2. R. S. Mulliken, *Nature, Lond.*, **122**, 505 (1928).
3. W. H. J. Childe and R. Mecke, *Z. Physik*, **68**, 344 (1931).
4. G. Herzberg, *Nature, Lond.*, **133**, 759 (1934).
5. H. Kautsky and H. de Bruijn, *Naturwissenschaften*, **19**, 1043 (1931).
6. H. Kautsky, H. de Bruijn, R. Neuwirth, and W. Baumeister, *Chem. Ber.*, **66B**, 1588 (1933).
7. H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).
8. G. O. Schenk, *Naturwissenschaften*, **35**, 28 (1948).
9. P. A. Leighton, *Photochemistry of Air Pollution*, Academic Press, New York, 1961.
10. C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879 (1964).
11. E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, **86**, 3881 (1964).
12. A. M. Winer and K. O. Bayes, *J. Phys. Chem.*, **70**, 302 (1966); R. H. Kummelen, M. H. Bortner, and T. Baurer, *Environ. Sci. Technol.*, **3**, 248 (1969).
13. J. N. Pitts, Jr., A. U. Khan, E. B. Smith, and R. P. Wayne, *Environ. Sci. Technol.*, **3**, 241 (1969).
14. B. Rånby and J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, Wiley, London, 1975, Ch. 5.
15. A. M. Trozzolo and F. H. Winslow, *Macromolecules*, **1**, 98 (1968).
16. M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci. B*, **9**, 565 (1971).
17. M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci. A1*, **8**, 3163 (1970); *Rubb. Chem. Technol.*, **45**, 423 (1972).
18. J. F. Rabek and B. Rånby, *J. Polym. Sci. A1*, **14**, 1463 (1976).
19. J. F. Rabek and B. Rånby, *J. Polym. Sci. A1*, **12**, 273 (1974).
20. B. Rånby and J. F. Rabek, *Amer. Chem. Soc. Symp. Ser.*, No. 25, 391 (1976).
21. Chapters 10, 11, 15-18, 31, 32 of this volume.

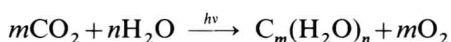
The Nature of Singlet Oxygen

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Although the oxygen atom accounts for less than 0.1% of the atoms in the universe, the forces which formed the earth some 5×10^9 years ago have made oxygen the most abundant element in the earth's crust, and it accounts for more than half the atoms now present. However, it is clear from the geological record that molecular oxygen was not an important species in the early planetary atmosphere.¹ On the contrary, the small amounts formed by the direct photolysis of inorganic oxides probably acted as a poison, destroying amino acids formed in the planets' 'Haldane soup'.²

The appearance of significant amounts of molecular oxygen in the atmosphere had to await the development of photosynthetic organisms capable of driving the process



This appears to have occurred in the sheltered depths of warm pools of water, when the earth was about half its present age.³ It is likely that the process was autocatalytic as protection from lethal ultraviolet radiation afforded by O_2 and O_3 undoubtedly led to the rapid spread of life out of the deep waters in which they originated. Exposure to oxygen at these higher levels would have caused organisms which based their metabolism on anaerobic photoreduction and fermentation to change to photosynthesis and respiration.³

The explosion of life forms associated with an increase of oxygen to something approaching 1% of our present level has been identified with the Cambrian period some 600 000 000 years ago.³ A build-up of the O_2 to about 10% of the present concentration together with the associated O_2 layer would have reduced the UV radiation to non-lethal levels outside water, and have made possible the movement of life forms to dry land. Whether the O_3 level simply rose to something like the present level, or overshot, causing an ice-age or two, is still open to debate. However, it is evident that present levels of O_2 are the result of a dynamic equilibrium maintained principally by the autotrophic and heterotrophic organisms. The autotrophs consume carbon dioxide and produce O_2 in the photosynthetic process while the heterotrophs consume O_2 (and organic matter) in respiratory processes. The balance between these organisms keeps the molar

fraction of oxygen in the atmosphere at a remarkably constant value of 0.2091. It has been estimated that all of the oxygen in the atmosphere passes through this photosynthetic cycle in 2000 years.³

Thus, molecular oxygen currently permeates the entire chemosphere and biosphere, playing a central role in the process by which radiation from the sun is used to sustain life on the surface of the earth.

Credit for the discovery of oxygen is usually given to both Scheele and Priestley, who independently isolated the species in about 1772, although Priestley still believed he had 'dephlogisticated air' as late as 1800. In 1811, Avogadro recognized that oxygen is a diatomic molecule and in 1848 Faraday demonstrated that it is unique among diatomic molecules with an even number of electrons: it is paramagnetic in its ground state. However, a satisfactory explanation of this paramagnetism was presented only in 1928 by Mulliken⁴ in what is considered a major triumph of molecular orbital theory. We will give the details of this description in a later section. For our present purposes it is sufficient to note that although O_2 has a 'double bond', its outermost pair of electrons are in different orbitals and have their spins parallel, making the ground state a 'triplet' ($^3\Sigma_g^-$). Furthermore, two other arrangements of these two electrons are possible and should result in the presence of two low-lying singlet states ($^1\Delta_g$ and $^1\Sigma_g^+$). Three years after Mulliken's classic paper, Childe and Mecke⁵ were able to verify these predictions with the spectroscopic observation of the $^1\Sigma_g^+$ state 37.51 kcal above the ground state, and in 1934 Herzberg reported the observation of the $^1\Delta_g$ state.⁶ It is this singlet delta state ($O_2\ ^1\Delta_g$) which has come to be called singlet oxygen. It lies only 22.54 kcal above the ground state and has a remarkable lifetime of 1 h in the absence of collisions with other molecules.

The role of singlet oxygen in a variety of photo-oxygenation processes has been demonstrated by many workers in the last 14 years but the literature reveals that in the period between 1931 and 1964 singlet oxygen had only one champion: Hans Kautsky,⁷⁻⁹ who in 1931 correctly proposed that this species is responsible for the photo-oxygenation of a variety of unsaturated molecules. With hindsight, it seems remarkable that Kautsky's beautiful experiments and careful reasoning did not convince his contemporaries. Although his papers continued to point to the importance of singlet oxygen throughout the 1930s, a moloxide mechanism for photo-oxygenation proposed in 1935 by Schönberg¹⁰ appeared more attractive to chemists. This alternative theory received the support of workers who dominated the field¹¹ and hence singlet oxygen was considered unimportant in the oxygenation of organic compounds until 1964 when the experiments of both Foote and Wexler¹² and Corey and Taylor¹³ provided new evidence for a singlet oxygen mechanism in several photo-oxygenations. Since then a great deal has been learned about the properties of the molecule and it is now becoming possible to assess its importance in a number of more complex systems such as polymer degradation.

The most universal and probably the more important mechanism by which singlet oxygen is formed in the earth's biosphere is the following. The absorption

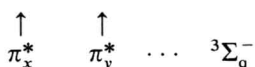
of visible and ultraviolet light (from the sun) usually leads to the electronic excitation of the molecules. Since oxygen permeates most organic matter, O_2 is a common quencher of this electronic excitation. In this process (especially when the excited state is a triplet), singlet oxygen is formed. Whether the species plays a significant role in such a system is determined by the rate of reaction with the molecules present relative to the rate of relaxation to the ground state. To understand these two processes we must consider the electronic structure of singlet oxygen and how it is affected by interactions with other molecules.

THE QUANTUM MECHANICAL DESCRIPTION OF SINGLET OXYGEN

The potential energy curve for singlet oxygen $O_2(^1\Delta_g)$ is given by the solid curve in Figure 1 together with the curves for the other two double-bonded states which arise from the LCAO-MO configuration:

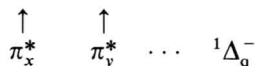
$$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$$

Because the σ bond in O_2 remains intact in the reactions which interest us, we can ignore all electrons except the six which are found in π orbitals. Four of these electrons fill the degenerate bonding π_x and π_y orbitals and two electrons half-fill the degenerate antibonding π_x^* and π_y^* orbitals. It is the arrangement of these two electrons in the antibonding orbitals that determine which of the three low-lying states shown in Figure 1 we have. The ground state is well represented by the following conventional diagram:

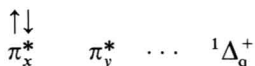


since the two electrons must be in different orbitals with their spins parallel to yield a ${}^3\Sigma_g^-$ state.

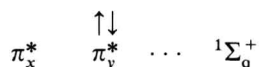
The singlet oxygen state is more difficult to represent in this manner.¹⁴ It is two-fold degenerate. One component, ${}^1\Delta_g^-$, has the two electrons in different orbitals and can therefore be represented by the diagram



However, this cannot be the component responsible for the interesting reactivity of singlet oxygen. The other component, Δ_g^+ , can be represented by



since the wave function indicates that both electrons are in the same orbital.¹⁴ Inspection of the orbital wave function for the ${}^1\Sigma_g^+$ state indicates that it also has the electrons paired. Therefore, we can represent it with the diagram



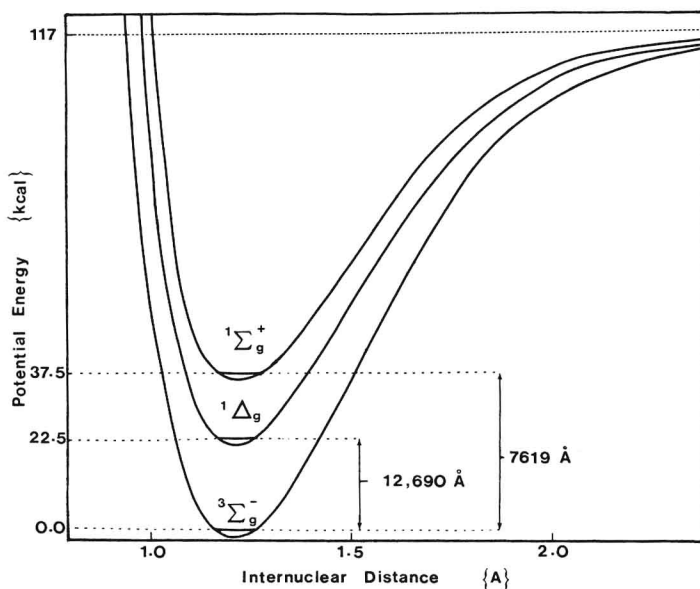


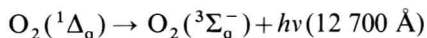
Figure 1 Potential energy curves for the three low-lying electronic states of molecular oxygen

The above representations of the ${}^1\Delta_g^+$ and ${}^1\Sigma_g^+$ states are valid only if the x -axis is chosen differently for electrophilic and nucleophilic reactants. This is necessary because any interaction stabilizes the ${}^1\Delta_g^+$ component of the ${}^1\Delta_g$ state and destabilizes the ${}^1\Sigma_g^+$ state relative to the ${}^1\Delta_g^-$ and ${}^3\Sigma_g^+$ states. Consequently, when an electrophilic species approaches $O_2({}^1\Delta_g)$ it 'points' its filled π_x^* orbital at the species, giving rise to a stabilizing interaction, whereas $O_2({}^1\Sigma_g^+)$ directs its empty orbital at the electrophile, producing a repulsive interaction.

It should be emphasized that the above description is a chemical interpretation of a general quantum mechanical result in perturbation theory calculations which is often described as a 'repulsion' between states which are mixed by a perturbation. It therefore does not take into account other possible interactions that are capable of shifting the positions of the ground state and the other component of the singlet delta state which have wave functions characteristic of free radicals. Nevertheless, there is little doubt that when singlet oxygen shows a high reactivity relative to the ground state it is the ${}^1\Delta_g^+$ component which is responsible. On the other hand, we would not expect $O_2({}^1\Sigma_g^+)$ to react as a free radical or undergo processes similar to $O_2({}^1\Delta_g)$. The fact that $O_2({}^1\Sigma_g^+)$ is readily relaxed to $O_2({}^1\Delta_g)$ could, however, lead to an observed reactivity when the ${}^1\Sigma_g^+$ state is formed as the first species in any system.

THE LIFETIME OF SINGLET OXYGEN

Isolated molecules of oxygen in the $^1\Delta_g$ state spontaneously undergo a transition to the ground state, principally through the transition:

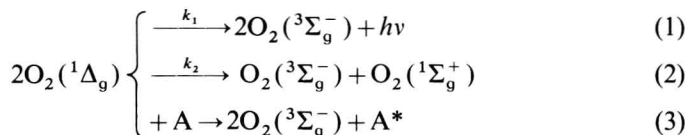


for which $k = 0.935\text{ h}^{-1}$ or the half-life is 45 min.¹⁵ This is a magnetic dipole transition. Collisions with other molecules can shorten this lifetime in two ways: (a) they can induce an electric-dipole transition at the same wavelength; (b) they can induce a radiationless transition to the ground state. For example, in the presence of 1 atm of O_2 the radiative half-life becomes 10 min¹⁵ and the non-radiative half-life becomes 14 ms. This makes the dark process almost 10^4 times faster than the radiative process. It is clear that radiative decay will not determine the actual lifetime of singlet oxygen below the stratosphere. However, it is worth noting that this shortening of the radiative lifetime in collisions means that a given 12 700 Å emission intensity from solution is indicative of a much smaller singlet oxygen concentration than the same intensity from the gas phase.

The ability of molecules to quench singlet oxygen in the gas phase and in solution is the subject of several papers in this volume, and exact rate constants are available for many quenchers. From these values we learn that in the gas phase at 1 atm the lifetime of singlet oxygen can vary between 1 and 10^{-5} s, depending on the nature of the gas. In solution the lifetime varies between 1 ms (in Freon 11) and 2 μs (in water) at room temperature. The mechanism of the relaxation in both phases is reasonably well understood and can be used to predict lifetimes in new media.^{16,17}

COOPERATIVE TRANSITIONS AND ENERGY POOLING

Spectroscopic studies of singlet oxygen generated both chemically and electrically have revealed some novel radiative and energy disproportionating processes.¹⁸⁻²¹ It was found that pairs of singlet oxygen molecules could combine their electronic excitation to bring about processes which require the energy from up to four molecules of $\text{O}_2(^1\Delta_g)$. The most important of these are described by the following equations:

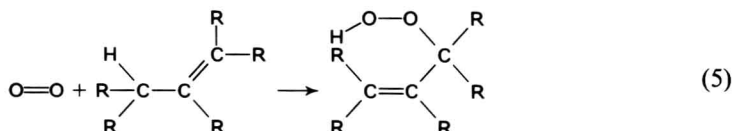
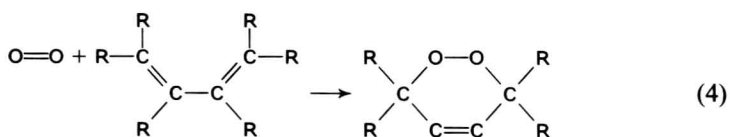


The first process gives rise to the so-called 'dimol' emission at 6340 Å and 7030 Å which is proportional to the square of the $\text{O}_2(^1\Delta_g)$ concentration, $k_1 = 0.28\text{ l mol}^{-1}\text{ s}^{-1}$. Emission from this cooperative transition provided the first direct evidence for chemically generated singlet oxygen in the chlorine-peroxide reaction.¹⁸ The same transition has also been used to excite singlet

oxygen, providing direct evidence for some singlet oxygen reactions.²² The second process [equation (2)] can be considered an energy disproportionation and is possible because the energy of two singlet delta molecules (45 kcal) is sufficient to excite the singlet sigma state (37.5 kcal), $k_2 = 1.3 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$. One consequence of this process is the presence of small amounts of the higher singlet state when the lower (delta) state is formed.¹⁹ The third process [equation (3)] was proposed to account for the luminescence from aromatic molecules excited by singlet oxygen.^{20,23} The detailed mechanism by which such co-operative excitation occurs is still controversial.

STATE CORRELATION DIAGRAMS

The two principal reactions characteristic of singlet oxygen are cycloaddition and the 'ene' reaction [reactions (4) and (5), respectively]:



The formation of endoperoxides shown in reaction (4) requires a conjugated double bond. The formation of hydroperoxides as shown in reaction (5) requires an allylic hydrogen. When the double bonds are surrounded by electron-donating groups, the activation energy for both reactions can be reduced to nearly zero and the rate constant then approaches its maximum value of about $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.²⁴ The formation of dioxetanes in singlet oxygen reactions appears to have a much higher activation energy and is observed chiefly when other paths are blocked.^{25,26} This is consistent with the predictions of the Woodward-Hoffman selection rules for concerted cycloaddition reactions.²⁷ Such orbital symmetry considerations and more quantitative calculations²⁷ indicate that the $^1\Delta_g^+$ component is the only one which correlates directly with the ground-state products in reaction (4). These correlations are illustrated by the potential energy curves shown in Figure 2. It is likely that the curves also apply to the 'ene' reaction since there is a topological similarity between the two processes. They show similar rate constants, temperature dependences and variations with substituents around the double bond(s). It has also been suggested that peroxirane intermediate may be important in the 'ene' reaction.²⁷ Although such an intermediate has not been identified, some MINDO/3 calculations by Dewar and Thiel support this possibility.²⁸ Potential energy curves based on these calculations are presented in Figure 3 and remain