be arranged in the order of a progressive change, for example, as Figures 4b, 4c (or 5a), and 5d, from a very qualitative point of view. It is possible that this progressive change in line shape may be coherently interpreted in terms of the relative energy values of zero-field splitting (D) and interdimer spin-exchange interaction (J'); namely, $|D| \gg |J'|$ in Figure 4b, $|D| \sim |J'|$ in Figure 4c, and $|D| \ll |J'|$ in Figure 5d, where $|D|$ is of the order of 0.1–0.05 cm^{-1} for the present complexes. The types of powder ESR line shapes for the other green complexes are summarized in Table I using these spectra as standards for comparison. No correlations between the line shape and N-alkyl group, however, can be detected in this table. From the fact that all the green complexes show various ESR line shapes, in spite of their structures being almost the same, it is suggested that drastic changes in ESR line shape for this series of complexes are brought about by small changes in crystal structure, and that these complexes are interesting samples suitable for the investigation of intermolecular spin-exchange interaction in crystals. More quantitative investigations on these problems are now in progress, with the help of crystal structural determinations and single-crystal ESR studies.

References and Notes

(1) H. Yokoi, M. Otagiri, and T. Isobe, *Bull. Chem. Soc. Jpn.*, **44**, 2395, 2402 (1971); *ibid.*, **48**, 442 (1973); H. Yokoi, unpublished results.
(2) H. Yokoi, *Chem. Lett.*, 1023 (1973).
(3) T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, **13**, 173 (1974), and the references therein.
(4) M. Chikira and T. Isobe, *Bull. Chem. Soc. Jpn.*, **45**, 3006 (1972).
(5) M. Chikira and T. Isobe, *Chem. Lett.*, 865 (1974); *Chem. Phys. Lett.*, **30** 498 (1975).
(6) P. Pfeiffer, E. Buchholz, and O. Bauer, *J. Prakt. Chem.*, **129**, 163 (1931); P. Pfeiffer and H. Glaser, *ibid.*, **153**, 265 (1939).
(7) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).
(8) Z. Matsumura, M. Chikira, S. Kubota, and T. Isobe, *Rev. Sci. Instrum.*, **45**, 596 (1974).
(9) P. W. Selwood, "Magnetochemistry", Interscience, New York, N.Y., 1956, Chapter 6.
(10) K. Shibata, "Methods of Biochemical Analysis", Vol. 7, D. Glick, Ed., Interscience, New York, N.Y., 1959, p 77; Vol. 9, 1962, p 217; H. Yokoi, M. Sai, T. Isobe, and S. Ohsawa, *Bull. Chem. Soc. Jpn.*, **45**, 2189 (1972).
(11) B. Bleaney and K. D. Bowers, *Proc. R. Soc., London, Ser. A*, **214**, 451 (1952).
(12) M. Chikira, H. Yokoi, and T. Isobe, *Bull. Chem. Soc. Jpn.*, **47**, 2208 (1974).
(13) D. Hall, S. V. Sheat, and T. N. Waters, *J. Chem. Soc. A*, 460 (1968).
(14) D. Hall, R. H. Summer, and T. N. Waters, *J. Chem. Soc. A*, 420 (1969); G. Bombieri, C. Panattoni, E. Forsellini, and R. Graziani, *Acta Crystallogr., Sect B*, **25**, 1208 (1969); the references in these papers.
(15) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 3910 (1969), and the references therein.
(16) M. Kato, K. Imai, Y. Muto, T. Tokii, and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, **35**, 109 (1973), and the references therein.
(17) Yu. V. Yablokov, V. A. Gaponenko, L. V. Mosina, V. A. Kogan, and T. A. Zhuchenko, *Zh. Strukt. Khim.*, **14**, 216 (1973).
(18) H. Ohkawa, T. Tokii, Y. Nonaka, Y. Muto, and S. Kida, *Bull. Chem. Soc. Jpn.*, **46**, 1462 (1973).
(19) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Metal Ions", Clarendon Press, Oxford, 1970.
(20) H. S. Jarrett, *J. Chem. Phys.*, **28**, 1260 (1958).
(21) W. E. Hatfield, *Inorg. Chem.*, **11**, 216 (1972).
(22) J. F. Villa and W. E. Hatfield, *Inorg. Chem.*, **11**, 1331 (1972).

Ground States of Molecules. XXX. MINDO/3 Study of Reactions of Singlet ($^1\Delta_g$) Oxygen with Carbon–Carbon Double Bonds[1,2]

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Abstract: The reactions of singlet ($^1\Delta_g$) oxygen with carbon–carbon double bonds have been studied using MINDO/3. The compounds examined were ethylene, propene, vinylamine, and 2,3-dihydropyran. The reactions are predicted to take place in steps via peroxirane or zwitterionic intermediates. The results are consistent with the available experimental evidence.

During the past decade, it has been established that singlet ($^1\Delta_g$) oxygen is the reactive intermediate in the photooxygenation of alkenes as well as in oxidations brought about by the hypochlorite–hydrogen peroxide system.[3-5]

Three modes of reaction have been observed with alkenes:[6-10] 1,2-cycloadditions to yield dioxetanes; the ene reaction to form allylic hydroperoxides; and 1,4-cycloadditions with dienes leading to endoperoxides. The mechanisms of these reactions are the subject of much current controversy, the main question being whether the reactions are concerted or involve intermediates.

For a concerted 1,2-cycloaddition, both a $({}_{\pi}2_s + {}_{\pi}2_s)$ and a $({}_{\pi}2_s + {}_{\pi}2_a)$ process have been considered theoretically.[8,11-13] State correlation diagrams[8,11,12] and orbital-phase continuity arguments[13] suggest that the $({}_{\pi}2_s + {}_{\pi}2_s)$ approach should be "forbidden", although it has been proposed[8] that this process might occur in the case of alkenes with particularly low ionization potentials. The $({}_{\pi}2_s + {}_{\pi}2_a)$ approach is classified as symmetry allowed[8,13] and has therefore been considered a likely pathway for dioxetane formation.[13,14]

Stepwise 1,2-cycloaddition could occur via peroxiranes[8,12] or zwitterionic species.[14-16] Experimental evidence for the intermediacy of peroxiranes in the photooxygenation of 2,5-dimethyl-2,4-hexadiene[17] and of 2,2′-biadamantylidene[18] has recently been reported. Correlation diagrams[8,12] and consideration of frontier orbital interactions[19] indicate that peroxirane formation is an allowed process. Zwitterionic intermediates should be important only in the case of electron-rich alkenes such as enamines[16] or enol ethers.[14,15] A recent theoretical study has described the photooxygenation of 2-aminopropene as a "symmetry-forbidden concerted" reaction proceeding via an essentially zwitterionic transition state.[13]

For the ene reaction, most authors favor a concerted mechanism in which the characteristic bond shifts take place via a cyclic transition state with a six-membered ring.[6,20] Others have proposed peroxiranes[21,22] or dioxetanes[11,23] as intermediates. The pathway via dioxetanes, however, was later ruled out by the observation that dioxetanes cleave to carbonyl compounds rather than rearrange to hydroperoxides.[24]

An experimental distinction between the two remaining possible mechanisms is difficult. The stereospecifity of the ene reaction,[5-7,20] the lack of substituent and solvent effects on product distribution,[5,9,25] and the futility of attempts to detect peroxirane intermediates[26] are usually taken as evidence for the concerted mechanism. Recently indirect evidence for a peroxirane intermediate has been obtained from a stereochemical study of the photooxygenation of (*R*)-(−)-*cis*-2-deuterio-5-methyl-3-hexene.[27]

Serious problems have clearly arisen in attempts to determine the mechanisms of these reactions by experimental studies because of the likely presence of intermediates that are too transient to be easily detected. This is the kind of situation where theoretical calculations should be of especial value, provided that they are carried out by a procedure accurate enough and reliable enough to be chemically significant. However, apart from some rather crude and inconclusive CNDO/2 calculations,[12] no theoretical investigation of the ene reaction has as yet been reported.

Recent work here has shown that the latest version (MINDO/3)[28] of the MINDO semiempirical SCF MO treatment[29-31] comes close to meeting these requirements, having given good results for a wide variety of molecules. We therefore decided to use it to study the reactions of $^1\Delta_g$ O_2 with olefins.

Theoretical Procedure

The MINDO/3 method has been discussed in detail in earlier papers of this series.[28] The calculations reported here were carried out using the parameters listed in Part XXV.[28] Geometries of molecules were found by minimizing their total energy with respect to all geometrical variables, using a program[32] based on the Davidon–Fletcher–Powell algorithm.[33] Structures of transition states were determined by the method of McIver and Komornicki[34-36] in which stationary points on the potential surface are found by minimizing the norm of the gradient. Transition states can be distinguished from other stationary points by the fact that they have only one negative eigenvalue of the force constant matrix and that their transition vector corresponds to the vibration which transforms the reactants into the products. By diagonalizing the force constant matrix, we confirmed that all the transition states reported here met these two conditions.[37]

A successful search for a transition state by gradient minimization requires a starting geometry close to the transition state. In order to generate such a starting point, we first investigated each reaction by the usual reaction coordinate procedure. In this, some coordinate (q) which varies monotonically during the reaction is taken as a reaction coordinate, the energy of the system being minimized with respect to all other coordinates for successive values of q. The maximum in the plot of energy vs. q usually approximates the transition state quite well and can be used as the starting point in the search program. Sometimes, however, especially in the case of "forbidden" reactions, this method fails. We then chose a reactant-like and a product-like structure from a reaction path described above and generated ($N - 1$) intermediate points by varying all internal coordinates linearly in N steps from their initial (reactant-like) to their final (product-like) values. The norm of the gradient was calculated for each of these geometries, and the intermediate point which showed a minimum in the plot of the scalar gradient vs. N was taken as the starting point in the search program.[36] Finally, if there was no such minimum, the starting point was determined by a two-dimensional grid search using two different reaction coordinates.[38]

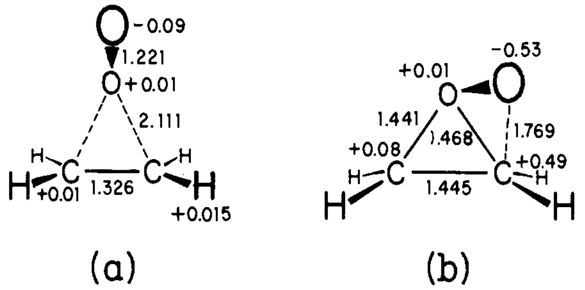


Figure 1. Calculated transition states (bond lengths in Å; formal charges in e) for (a) **1** + **2** → **3** (i.e., **5**); (b) **3** → **4** (i.e., **6**).

Results

Calculations were carried out for the reactions of $^1\Delta_g$ O_2 with ethylene, propene, vinylamine, and dihydropyran. The calculated heats of formation and other properties of the reactants, products, stable intermediates, and transition states are given in Schemes I–IV and Figures 1–4.

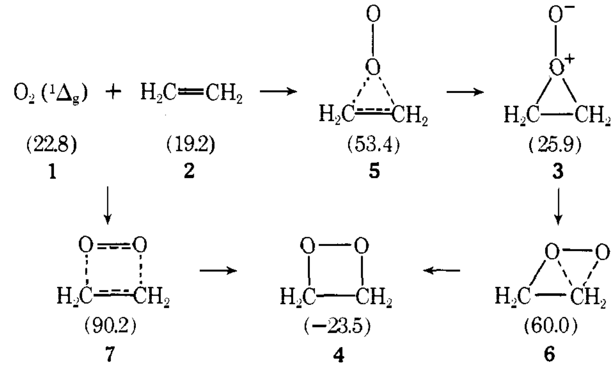
Since there is a possibility that some of the reactions might involve biradicaloid intermediates,[39] we repeated the calculations for the species studied, including configuration interaction with the lowest doubly excited configuration.[40] The corresponding decreases in energy were small, usually 2–3 kcal/mol,[41] implying that the species studied can be described by single-configuration wave functions for which MINDO/3 has been parametrized. All present results therefore refer to single-determinantal ground state calculations.

Since MINDO/3 gives a value for the heat of formation of oxirane that is too negative by 14 kcal/mol, it is likely that a similar error applies to the calculated heats of formation of peroxiranes. The calculated heats of formation of dioxetanes may also be too negative; here, however, no data for appropriate model compounds are available.

A. Reaction of $^1\Delta_g$ O_2 with Ethylene. The reaction of singlet oxygen with ethylene (see Scheme I), although not yet experimentally observed, is of special interest, because it provides the simplest example of a 1,2 cycloaddition of oxygen with no competing side reactions.

According to MINDO/3, the lowest energy approach of singlet oxygen (**1**) to ethylene (**2**) leads to the formation of peroxirane (**3**) with an activation energy of 11.4 kcal/mol. The transition state (**5**) for this addition has a reactant-like C_s structure (Figure 1a). The CC and OO bond lengths are increased by only 0.012 and 0.015 Å, respectively, relative

Scheme I[a]



[a] Calculated heats of formation (kcal/mol) in parentheses.

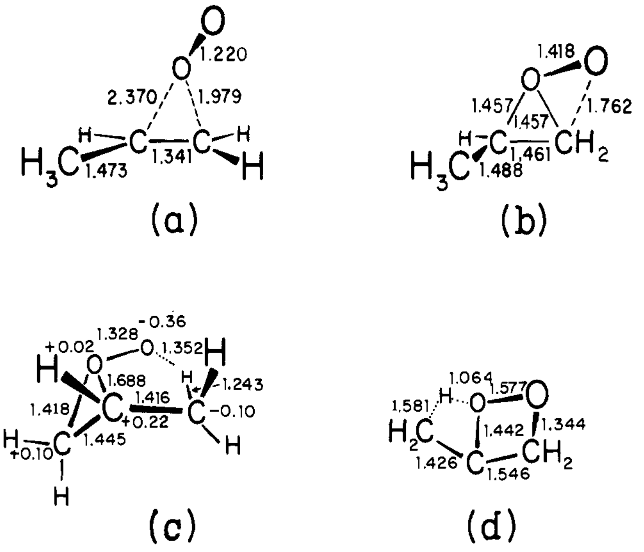


Figure 2. Calculated transition states (bond lengths in Å; formal charges in e) for (a) **1** + **8** → **9a** (i.e., **10a**; the structure of **10b** is similar); (b) **9a** → **11** (i.e., **12a**; the structure of **12b** is similar); (c) **9a** → **14** (i.e., **13**); (d) **11** → **14** (i.e., **15**).

to their values in free ethylene and singlet oxygen. The electronic interaction between the ethylene and oxygen moieties in **5** is seen to be very weak both from the low CO two-center energy[42] of −0.8 eV and from the small amount of net charge (−0.08 e) transferred to O_2.

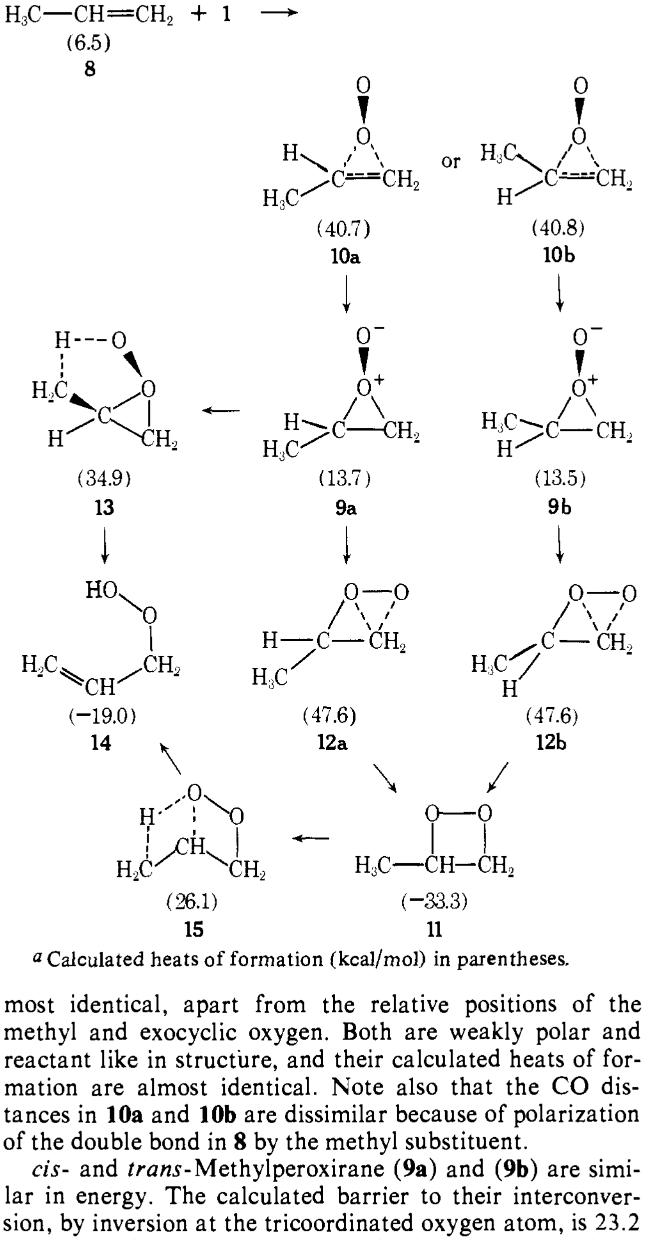
Peroxirane (**3**) also assumes a symmetrical C_s structure, with an angle of 127° between the OO bond and the plane of the ring. It is a very polar molecule with a dipole moment of 4.26 D, the external oxygen atom carrying a large negative charge (−0.48 e). Peroxirane rearranges to 1,2-dioxetane (**4**) via a very unsymmetrical transition state (**6**) (Figure 1b) which still contains the three-membered ring and indeed resembles peroxirane. In **6**, the two-center energy[42] of the breaking CO bond (E_{CO} = −9.2 eV) is only slightly lower than that for the remaining CO bond (E_{CO} = −11.1 eV). Evidently **6** is a dipolar species because the carbon and oxygen atom which form the new bond bear large opposite charges (+0.49 and −0.53 e, respectively). In the 1,2 cycloaddition, **6** is the rate-determining transition state, because it lies 6.6 kcal/mol above **5** in energy.

These results established the feasibility of a two-step pathway for the formation of 1,2-dioxetane. Next we looked to see whether there might be a competing concerted process. We first investigated symmetrical approaches of ethylene to oxygen, taking the distance between the midpoints of the CC and OO bonds as the reaction coordinate. Imposing C_{2v} symmetry [($_\pi 2_s$ + $_\pi 2_s$) approach], no continuous transformation between reactants and products took place. This reaction is "forbidden", because the π_{CC} a_1-HOMO in ethylene does not correlate with the π^*_{OO} a_2-HOMO in 1,2-dioxetane. Reducing the symmetry to the C_2 point group [($_\pi 2_s$ + $_\pi 2_a$) approach], the reaction becomes formally allowed, because both relevant MO's are symmetrical with respect to the C_2 axis. In the reaction path under C_2 symmetry, the carbon and oxygen atoms assumed a planar C_{2v} configuration for values of the reaction coordinate R below 1.8 Å and above 2.0 Å. Between 1.8 and 2.0 Å, the OO bond was twisted relative to the CC bond, allowing an effective mixing of the π_{CC}- and π^*_{OO}-MO's. A stationary point **7** with C_2 symmetry was indeed found on the potential surface, with R = 1.829 Å and a dihedral angle of 29° between the CC and OO bonds. This structure, however, had *two* negative eigenvalues of the force constant matrix and therefore does *not* qualify for a transition state.[34]

While these results rule out a symmetrical concerted cycloaddition, there might still be an unsymmetrical concerted pathway. The heat of formation for our system was therefore calculated as a function of the bond lengths R_1 and R_2 of both forming CO bonds (R_1 varied between 1.4 and 2.2 Å; R_2 varied between R_1 and R_1 + 1.2 Å, intervals of 0.1 Å), all other variables being optimized. In this grid search, no evidence for a one-step cycloaddition could be detected. In the region of interaction ($R_1 \geq 1.8$ Å and $R_2 \geq 1.8$ Å), structures which are geometrically and electronically similar to peroxirane were always more stable than dioxetane-like structures. Therefore we have to conclude that, according to MINDO/3, the cycloaddition of singlet oxygen to ethylene proceeds exclusively by formation of a peroxirane intermediate which rearranges to 1,2-dioxetane.

B. Reaction of $^1\Delta_g$ O_2 with Propene. As in the case of ethylene, the approach of $^1\Delta_g$ O_2 to propene (**8**) yields methylperoxirane as the first product. This can be formed in cis (**9a**) or trans (**9b**) geometries. The structures of the corresponding transition states (**10a** and **10b**; Figure 2a) are almost identical, apart from the relative positions of the methyl and exocyclic oxygen. Both are weakly polar and reactant like in structure, and their calculated heats of formation are almost identical. Note also that the CO distances in **10a** and **10b** are dissimilar because of polarization of the double bond in **8** by the methyl substituent.

Scheme II[a]



[a] Calculated heats of formation (kcal/mol) in parentheses.

cis- and *trans*-Methylperoxirane (**9a**) and (**9b**) are similar in energy. The calculated barrier to their interconversion, by inversion at the tricoordinated oxygen atom, is 23.2 kcal/mol. The barrier to inversion in the 1-isopropyloxiranium ion has been estimated (NMR) to be 10 ± 2 kcal/

mol.[43] The higher value for methylperoxirane is reasonable, because introduction of electronegative substituents is known to increase inversion barriers appreciably.[44]

Both **9a** and **9b** can rearrange, like **3**, to the corresponding dioxetane **11** via very unsymmetrical and quite highly polar transition states **12a** and **12b** (Figure 2b). The rearrangement takes place most easily in the manner indicated, the exocyclic oxygen becoming attached to the unsubstituted carbon. If it moves to the substituted carbon, the corresponding transition states are higher in energy by 1.2 (trans) and 3.0 kcal/mol (cis), probably because of an increase in nonbonded interactions.

The presence of the methyl group in *cis*-methylperoxirane (**9a**) allows an alternative mode of rearrangement via the cyclic transition state **13** (Figure 2c) to form the "ene" product, propene-3-hydroperoxide (**14**). In **13** the breaking CH bond is still rather strong (bond length 1.243 Å; two-center energy −8.2 eV) and the forming OH bond still very weak (bond length 1.352 Å; two-center energy −4.1 eV). Comparing the calculated heats of formation for the various transition states, **13** is lower in energy than **10a** or **12a** by 5.9 and 12.7 kcal/mol, respectively. Thus MINDO/3 predicts that the intermediate methylperoxirane should rearrange more easily to the hydroperoxide (ene reaction) than decompose or rearrange to the dioxetane (1,2 cycloaddition).

Hydrogen migration in methyl-1,2-dioxetane (**11**) could provide another pathway to the hydroperoxide (**14**). The corresponding transition state (**15**; Figure 2d) has a distorted boat-like structure in which the four-membered ring is still preserved. In contrast to the hydrogen migration in **9a**, the breaking of the CH bond and the forming of the OH bond are far advanced in **15**, as can be seen from the calculated bond lengths (CH, 1.583 Å; OH, 1.064 Å) and two-center energies[42] (CH, −3.7 eV; OH, −7.3 eV). The MINDO/3 results imply that hydrogen migration in the dioxetane cannot play any role in the ene reaction between propene and singlet oxygen for the following reasons. First, the rate-determining transition state for the ene reaction has a heat of formation of 40.8 kcal/mol via the peroxirane route but 47.6 kcal/mol via the dioxetane route. Secondly, even if the dioxetane were formed, the hydrogen migration in **11** requires a calculated activation energy of 59.5 kcal/mol. On the other hand, MINDO/3 predicts[45] that 1,2-dioxetane decomposes into two molecules of formaldehyde, one of which is produced in the triplet state, with an activation energy of 38.3 kcal/mol. A similar value is expected for **11** so, if it is formed, it should decompose rather than rearrange to **13.**

MINDO/3 thus describes the ene reaction as a two-step process via a peroxirane intermediate. In attempts to find a competing one-step process, a two-dimensional potential surface for the reaction was calculated. The bond lengths R_{CO} and R_{OH} of the forming CO and OH bonds were taken as independent variables, all other internal coordinates being optimized (R_{CO} varied between 1.4 and 3.0 Å, R_{OH} between 1.4 and 2.4 Å, intervals of 0.2 Å). In this grid search, no path for a one-step ene reaction was found. The only valleys in the surface corresponded to the two-step mechanism described above.

The rate-determining transition state **10a** for the ene reaction is predicted to be 11.5 kcal/mol higher in energy than the reactants. Experimental data are not yet available for the reaction between propene and singlet oxygen. The calculated activation energy, however, is in excellent agreement with the experimental value for *cis*-butene[46] (10.0 ± 1.0 kcal/mol), considering that the substitution of one methyl group by a hydrogen atom should slightly increase the activation energy.

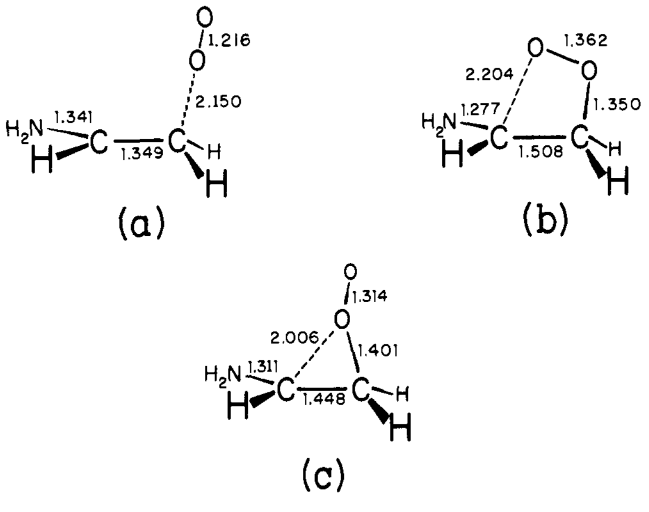
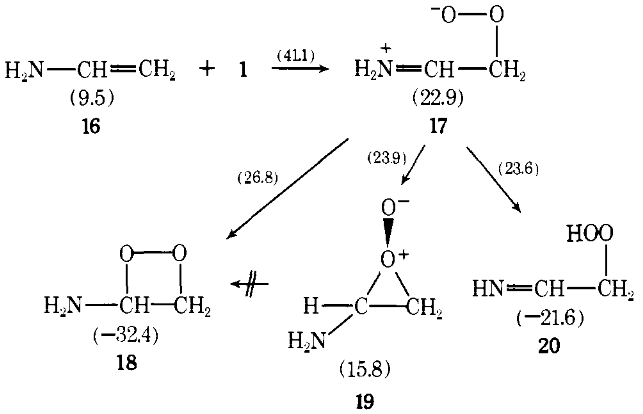


Figure 3. Calculated transition states (bond lengths in Å) for (a) **1** + **16** → **17**; (b) **17** → **18**; (c) **17** → **19.**

C. Reaction of $^1\Delta_g$ O_2 with Vinylamine. Vinylamine (**16**) and its tautomer iminoethane (HN=CHCH$_3$) are unstable species with regard to polymerization. Naturally this does not prevent us from using vinylamine as a model substrate for the 1,2 cycloaddition of singlet oxygen to tertiary enamines.[16,47]

According to MINDO/3, singlet oxygen adds to vinylamine to form the zwitterion **17** rather than a peroxirane. The transition state for this process is very similar to the reactants in structure and only weakly polar (Figure 3a). The zwitterion occupies a very shallow minimum in the potential surface from which it can escape in several ways.

Scheme III[a]



[a] Calculated heats of formation (kcal/mol) of compounds, and of transition states for reactions, in parentheses.

First, it can undergo cyclization to the dioxetane (**18**) with an activation energy of 3.9 kcal/mol via a highly polar transition state (Figure 3b). Secondly, it can undergo cyclization to the *cis*-peroxirane (**19**) with an activation energy of 1.0 kcal/mol; the corresponding transition state is shown in Figure 3c. Thirdly, hydrogen migration from the amino group to oxygen can lead to the hydroperoxide **20;** this last reaction is not of much interest since enamines are not usually stable unless tertiary. It is predicted to be the most facile of the three (ΔE^+, 0.7 kcal/mol).

The activation energy for rearrangement of **19** to **18** is predicted to be much higher than that for formation of **18** from **16** via **17.** Apart from the trivial formation of **20,** the peroxirane has therefore no escape. According to our calculations, **19** should be more stable than the zwitterion (**17**) by 7.1 kcal/mol. Since, however, MINDO/3 seems to over-

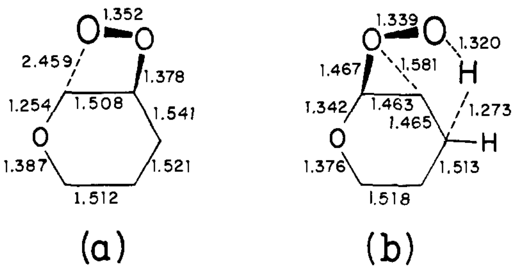


Figure 4. Calculated transition states (bond lengths in Å) for (a) **22** → **24**; (b) **23** → **25**.

estimate the stability of oxiranes by more than this, it seems likely that the conversion of **17** to **19** is in fact endothermic. If so, the peroxirane will play no role in the reaction, for, even if it is formed, it will simply revert to the zwitterion and end up as the dioxetane (**18**). Since the transition state for cyclization of **17** to **18** lies below that for formation of **17**, the latter should be the rate-determining step.

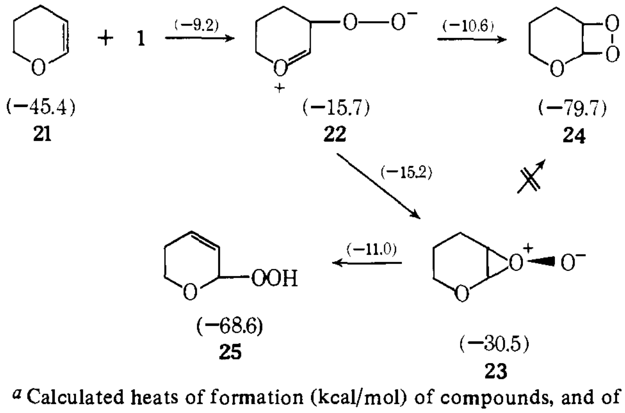
D. Reaction of $^1\Delta_g$ O_2 with Dihydropyran. Dihydropyran (**21**) is interesting in that it has been reported[48] to give *both* a dioxetane and an ene product on reaction with $^1\Delta_g$ O_2. Scheme IV summarizes our MINDO/3 studies.

Dihydropyran, like vinylamine, reacts with $^1\Delta_g$ O_2 to form a zwitterion (**22**), again via a reactant-like transition state of low polarity. The zwitterion can likewise undergo cyclization to a peroxirane (**23**) or a dioxetane (**24**), and the rearrangement of the peroxirane (**23**) to the dioxetane (**24**) is again a high-energy process; **24** is therefore formed only by cyclization of **22**. The transition state for this (Figure 4a), like that for formation of **18** from **17**, has an "open" zwitterionic structure with a very high dipole moment (8.59 D).

There is, however, an important difference between this system and vinylamine in that the peroxirane (**23**) now has a methylene group adjacent to the peroxirane ring. It can therefore undergo rearrangement to the ene product **25**. The corresponding transition state (Figure 4b) resembles that (**13**) for the analogous rearrangement of *cis*-methylperoxirane, having a chair-like structure and a relatively low dipole moment (2.94 D).

Thus **22**, can undergo conversion to two different stable products, either directly to **24** or indirectly to **25**. The activation energies for these two processes are almost identical (5.1 and 4.7 kcal/mol, respectively) so **24** and **25** should be formed in comparable amounts, as appears to be the case.[48] Note also that the rate-determining step for the overall reaction is again the formation of the zwitterion. Since the transition state for this is relatively nonpolar, changes in the solvent should have little effect on the overall rate of conversion of **21**. However, the relative amounts of **24** and **25** in the product should vary markedly with polarity of the solvent since the transition states for their formation have widely different dipole moments (8.59 and 2.94 D, respectively).

Scheme IV[a]



[a] Calculated heats of formation (kcal/mol) of compounds, and of transition states for these interconversions in parentheses.

E. Summary of Theoretical Results. The calculations reported here lead to the following conclusions concerning the course of the reactions of $^1\Delta_g$ O_2 with olefins:

(a) All such reactions appear to be nonconcerted, involving peroxiranes or zwitterions as intermediates which occupy shallow minima on the potential surface. Most authors had previously assumed, on the basis of apparently good analogies, that these reactions are concerted pericyclic processes.

(b) In the initial step of the reaction, $^1\Delta_g$ O_2 adds to the olefin to form a peroxirane, unless −E substituents are attached to the double bond; in this case, a zwitterion is formed as the first intermediate.

(c) Peroxiranes undergo rearrangement to ene products extremely easily, rearrangement to dioxetanes requiring far more activation. Indeed, in the case of ethylene and propene, reversion of the peroxirane to (olefin + O_2) is easier than rearrangement to the dioxetane.

(d) The zwitterions differ from peroxiranes in undergoing facile ring closure to dioxetanes. They can also form peroxiranes with equal ease. If the resulting peroxiranes can in turn rearrange to the ene products, there should then be a competition between the ene reaction and formation of a dioxetane.

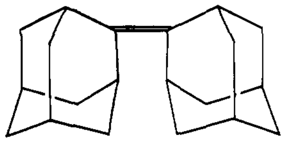
(e) Since the rearrangements of peroxiranes to ene products, and of zwitterions to dioxetanes, require very little activation, the lifetimes of these intermediates should usually be very short and they should therefore be hard to detect. The best hope of detecting or trapping such an intermediate should be in the case of an olefin that forms a peroxirane rather than a zwitterion and in which the peroxirane is unable to rearrange to an ene product.

Discussion

A. Comparison with Experiment. The conclusions reached in the previous section seem to provide a very satisfactory interpretation of the available experimental evidence.

Thus attempts to detect intermediates in these reactions have mostly been unsuccessful, the most notable exception being the photosensitized oxidation of 2,2′-biadamantylidene[18] (**26**), a tetraalkylethylene which cannot undergo the ene reaction (Bredt's rule). Oxidation in pinacolone **27** yielded not only the dioxetane **28** but also the oxirane **29** and *tert*-butyl acetate **30**, a result attributed to a Baeyer-Villiger type oxidation of **27** by an intermediate peroxirane **31**. A somewhat similar result has been reported[49] in the case of 7,7′-binorbornylidene (**32**), photooxidation of which gave the oxirane **33** in appreciable yields. In this case, however, the oxirane was also formed in solvents (e.g., methylene chloride and benzene) which are incapable of Baeyer-Villiger type reactions. If **33** was formed via the peroxirane **34**, reduction of the latter must have taken place in some other way.[50]

Further experimental evidence for peroxirane intermediates has been claimed[27] in the reaction of $^1\Delta_g$ O_2 with the rather unreactive olefin (*R*)-(−)-*cis*-2-deuterio-5-methyl-3-hexene (**35**). Studies of the stereochemistry of the resulting ene products and of their deuterium content seemed to support a stepwise mechanism via peroxiranes. Finally, we note that the predicted behavior of the peroxiranes is completely analogous to the observed reactions of alkyl-substituted aziridine *N*-oxides[51] which rearrange on heating to give allylhydroxylamines, not 1,2-oxazetanes.



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$H_3C—CO—C(CH_3)_3$

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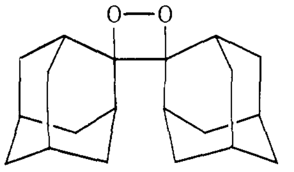

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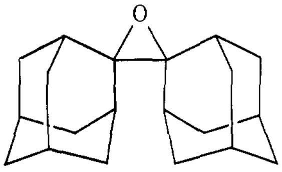

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$CH_3COOC(CH_3)_3$

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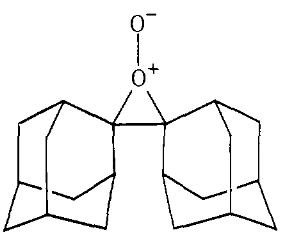

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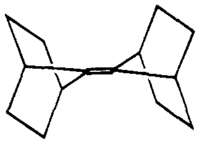

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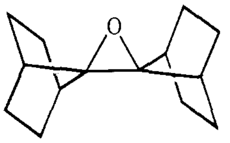

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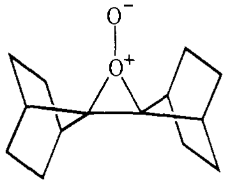

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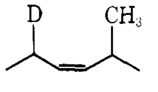

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Next let us consider reactions between $^1\Delta_g$ O_2 and olefins where there is at least one hydrogen α to the C=C double bond. As predicted by our calculations, the ene reaction is always found to be favored over the 1,2 cycloaddition whenever the ene reaction is possible. If the ene reaction cannot take place, most olefins (except tetraalkyl-substituted ones) do not react at all, because the activation energy for the peroxirane–dioxetane rearrangement is too high. A particularly interesting example is norbornene which fails to react with $^1\Delta_g$ O_2.[52] Since norbornene is rather susceptible to electrophilic attack, it seems quite likely that the peroxirane is formed. The ene reaction, however, is again barred by Bredt's rule; the peroxirane therefore reverts to the reactants, because this is easier than rearrangement to the dioxetane.

In cases where the peroxirane can rearrange to different ene products by abstraction of different hydrogen atoms, substituent effects seem to play no significant role in determining the product ratios.[5,9,25] This has been put forward as an argument against a stepwise mechanism, although it is not clear why it should not apply equally to a concerted pericyclic one. It will be seen that our calculated transition state **13** for the ene rearrangement of methylperoxirane strongly resembles methylperoxirane itself in structure, the breaking CH and CO bonds still being very strong and the nascent OH bond still very weak. Since the transition states for ene rearrangements are so similar to the reactant in structure, substituents should have little effect on their energies and hence on the relative rates of different modes of rearrangements. Our calculations are therefore entirely consistent with the experimental evidence.

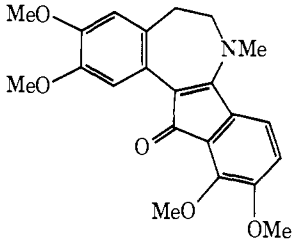
Similar remarks apply to the known stereospecifity of the ene reaction[5-7,20] since the two-step mechanism must lead to the same product as a concerted pericyclic process. Indeed, the calculated transition state **13** differs from that expected for a concerted reaction only in that the CO bond is already fully formed and by the presence of an additional CO interaction. Otherwise **13** has the same chair-type geometry that would be expected for the pericyclic transition state.

The measured intramolecular deuterium isotope effects for the photooxygenation of partly deuterated 2,3-dimethyl-2-butene[53,54] and bicyclohexylidene[53] are low, in the range between 1.2 and 2.0. These results are clearly to be expected on the basis of our calculations since, in the transition state for the peroxirane–hydroperoxide rearrangement (e.g., **13**), the breaking CH bond is still almost intact.

On the other hand, virtually no intermolecular deuterium isotope effect should be observed in a competitive photooxygenation of an olefin and its completely deuterated analog because, according to our calculations, the rate-determining step in the ene reaction is the formation of the peroxirane. This can be subject only to secondary deuterium isotope effects, which should moreover be unusually small, because the transition state for the addition of $^1\Delta_g$ O_2 to the double bond resembles the reactants in structure. Such a competition experiment has been reported[54] for *cis*- and *trans*-stilbene, the measured intermolecular deuterium isotope effect being 1.1 in both cases, with an estimated accuracy of 10%. Since 2,3-dimethyl-2-butene, which reacts much faster with $^1\Delta_g$ O_2 than the stilbenes do, shows an intramolecular isotope effect of 1.4 under similar conditions, these results seem to support the two-step mechanism that is predicted by MINDO/3.[55]

Turning now to the reactions of −E substituted olefins, these, as predicted, react very easily with $^1\Delta_g$ O_2 to form dioxetanes which can subsequently cleave to carbonyl derivatives. Such reactions have, for example, been observed with enamines,[16,47] enol ethers,[12,14,15,56,57] and thioenol ethers.[58,59] The 1,2 cycloaddition of $^1\Delta_g$ O_2 to enol ethers has been shown to be stereospecifically cis. A good example is provided by *cis*- and *trans*-1,2-diethoxyethylene[14] which give two different dioxetanes with $^1\Delta_g$ O_2. On the other hand, while *cis*-ethoxyphenoxyethylene gives exclusively cis addition, the trans isomer gives only 75–90% of cis adduct.[57] Our calculations account well for these results for, although the CC bond in the intermediate zwitterion is single, MINDO/3 predicts a high barrier to rotation because of Coulombic attraction between the positive and negative centers. The barrier to rotation is indeed higher than that for collapse to the dioxetane, which should therefore be formed stereospecifically or almost stereospecifically.

Initial formation of a zwitterionic intermediate should generally be considered in the photooxygenation of −E substituted olefins. In a recent study on the photosensitized oxidation of the enaminoketone **36**,[60] the first intermediate in the mechanism suggested is the dioxetane **37** which, how-



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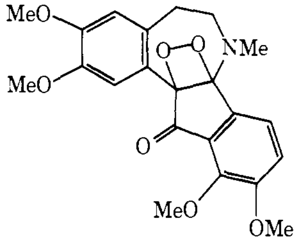

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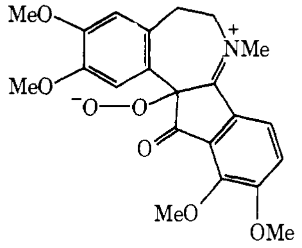
ever, might be expected to cleave in the usual way. This difficulty does not of course arise if the zwitterion **38** is formed



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initially. Moreover, the zwitterion should undergo the second step of the transformation[60] much more easily than the dioxetane.

The reported effects of solvents on the rates of these reactions are also easily interpreted in terms of our calculations. The rate-determining step in the ene reaction, and in the 1,2 cycloaddition to −E-substituted olefins, is the initial addition of oxygen to the olefin, and the calculated transition states have low dipole moments. One would therefore expect the overall rates to be little affected by changes in solvent, as indeed seems to be the case.[8,9] One would also expect the relative rates of reaction of two different olefins to be much the same in different solvents; this again is true, a particularly striking example being the pair 2,3-dimethyl-2-butene and 1,2-diethoxyethylene[14] which give quite different products (ene reaction and 1,2-cycloaddition, respectively).

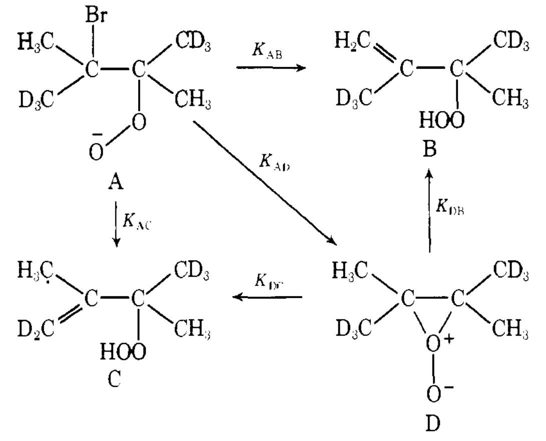
The calculated transition state for rearrangement of a peroxirane to an ene product is predicted to resemble the peroxirane both in structure and in polarity. Therefore in cases where different ene products can arise from a given olefin, their proportions should be similar in different solvents. This again appears to be the case, a good example being provided by a very detailed study of 2-methyl-2-pentene.[25]

The situation should, however, be quite different in the case of dihydropyran **21** which can give either the ene product **25** via a peroxirane **23** or the dioxetane **24** via a zwitterion **22.** Here the two product-forming transition states differ greatly in polarity, their calculated dipole moments being 2.9 and 8.6 D, respectively. An increase in the polarity of the solvent should now greatly alter the product ratio, favoring formation of the dioxetane **24.** The ratio **24**:**25** in fact increases by a factor of 58 on changing the solvent from benzene to acetonitrile.[48]

B. Peroxiranes in Related Reactions. β-Halohydroperoxides derived from tetraalkyl-substituted ethylenes are converted by base to allylic hydroperoxides, providing an alternative synthetic route to the products of the ene reaction.[54,61] The proposed mechanism for this conversion[54] involves an intramolecular substitution yielding a tetraalkyl-substituted peroxirane which then rearranges by hydrogen migration to the hydroperoxide. The peroxirane intermediate was postulated, because partial migration of the hydroperoxy group was observed, and because other mechanisms accounting for this migration could be ruled out. Different kinetic isotope effects were measured for the formation of the allylic hydroperoxide via the β-halohydroperoxide and via direct photooxygenation. It was therefore concluded that peroxiranes cannot be intermediates in the ene reaction.[54]

This argument would hold if the β-halohydroperoxide reaction took place entirely by a single mechanism. This, however, has not been established unambiguously,[62] and there is indeed a very reasonable alternative route from the bromohydroperoxide to the allyl hydroperoxide, i.e., an intramolecular EN2 elimination. Scheme V shows the possibility for the reactions in question. In the direct photooxidation, the product ratio B:C was found to be 1.4. If the reaction proceeds via the peroxirane, this implies that

Scheme V



$$K_{DB}/K_{DC} = 1.4 \qquad (1)$$

If we assume the stationary concentration of the peroxirane to be small, as must certainly be the case, then the ratio of B to C formed by reaction of A is given by eq 2. The ratio

$$\frac{[B]}{[C]} = \frac{K_{AB} + \dfrac{K_{AD}K_{DB}}{K_{DB} + K_{DC}}}{K_{AC} + \dfrac{K_{AD}K_{DC}}{K_{DB} + K_{DC}}} \qquad (2)$$

K_{AB}/K_{AC} is the isotope effect for a EN2 elimination. If we assume for this a value of 6, which is reasonable, and use eq 1 and 2, we obtain eq 3. Equating this to the observed ratio

$$\frac{[B]}{[C]} = \frac{{}^6\!/_7(K_{AB} + K_{AC}) + {}^7\!/_{12}K_{AD}}{{}^1\!/_7(K_{AB} + K_{AC}) + {}^5\!/_{12}K_{AD}} \qquad (3)$$

(2.1), we can find the proportions of A reacting by the EN2 and peroxirane routes, these being in the ratio $(K_{AB} + K_{AC}):K_{AD}$. The result is almost exactly 1:2. Therefore it seems reasonable to assume that both the ene reaction and the conversion of the bromohydroperoxy anion involve peroxirane intermediates, the latter reaction following in part a different course which explains the difference in the measured isotope effects.

C. Symmetry of Transition States. Until recently it was generally assumed that "allowed" pericyclic reactions in general, and "allowed" π cycloadditions in particular, take place in a symmetrical concerted manner. The discussion of such reactions in terms of conservation of state[63] or orbital[64] symmetry is indeed based on the assumption that elements of symmetry present in both reactant and product are retained during these interconversions. Recently, however, McIver[65] has shown that this cannot as a rule be the case for π cycloadditions; for the symmetrical structure, in which the lengths (R_1, R_2) of the two new σ bonds are equal, will have *two* negative eigenvalues of the force constant matrix so long as the force constants (K_{11} and K_{22}) for stretching of the two bonds in question are numerically greater than the corresponding cross constant K_{12}, a condition which will usually be fulfilled.

It has indeed recently been shown[66] here that some typical Diels-Alder reactions, according to MINDO/3, take place via very unsymmetrical transition states in which one of the new bonds is almost completely formed, the other hardly at all. The calculated structure **6** of the dioxetane-forming transition state in the 1,2 cycloaddition of $^1\Delta_g$ O_2

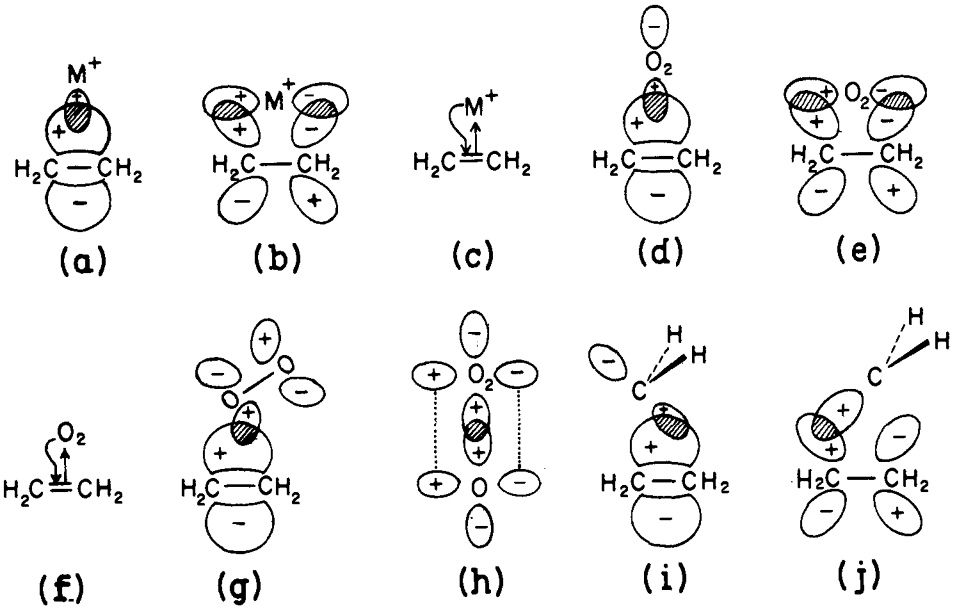


Figure 5. Formation of π complexes from ethylene (a–c) with a Lewis acid M^+ and (d–f) with $^1\Delta_g$ O_2; (g) unsymmetrical attachment of ethylene to $^1\Delta_g$ O_2 in the π complex; (h) formation of ozone from $^1\Delta_g$ O_2 + ^1D O; (i, j) unsymmetrical "allowed" approach of singlet carbene to ethylene.

to ethylene is likewise unsymmetrical, while the stationary point **7** for the "allowed" ($_{\pi}2_s$ + $_{\pi}2_a$) approach does not represent a transition state, because it has two negative eigenvalues of the force constant matrix and is higher in energy by 30.2 kcal/mol than the MINDO/3 transition state **6**.

It is therefore somewhat surprising that our calculated transition state **5** for peroxirane formation is symmetrical,[67] particularly since the apparently analogous "allowed" addition of carbene to ethylene involves an unsymmetrical approach.[68,69] This behavior can, however, be easily understood if we regard these reactions as electrophilic additions to olefins and discuss them in terms of the π complex theory.[70,71]

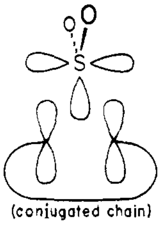
According to this, olefins can act as Lewis bases, using the filled bonding π MO to form a dative bond to any species with an empty valence orbital. If the acceptor also has a filled p, π, or d orbital at the atom through which it is attached to the olefin, this can be used for back-coordination by interaction with the empty antibonding π MO. This structure is illustrated in Figure 5a–c, the last using the notation suggested[71] for coordination and back-coordination. Typical apical groups are Br^+, $CH_2{=}CH^+$, and transition metal cations, back-coordination involving filled p, π, or d orbitals, respectively.

Now the π complex theory is based on the idea that either or both of the AO's used in forming a two-center bond can be replaced by MO's. Indeed, the original example was one where both AO's are so replaced.[72] In $^1\Delta_g$ O_2, the HOMO and LUMO are a pair of degenerate antibonding π MO's. These can clearly be used to form a π complex with ethylene, the filled bonding MO of ethylene interacting with the empty O_2 π MO and the filled O_2 π MO with the empty antibonding π MO of the ethylene; see Figure 5d–f. Both interactions will be greatest at all C_2–O_2 distances when the oxygen molecule lies on the perpendicular bisector of the CC bond. On the other hand, the ethylene must approach O_2 in an oblique manner, because the relevant MO's of O_2 are antibonding and so have nodes bisecting the OO bond (Figure 5g). The structure of the resulting π complex is indeed analogous to that of ozone, as can be seen by considering the formation of the latter by combination of $^1\Delta_g$ O_2 with a ^1D oxygen atom (Figure 5h).

This MO picture of a π complex in which the apical group is affected by a twofold interaction is equivalent[70,71] to a VB description with a three-membered ring. Presumably the force constants satisfy the McIver-Komornicki criterion for a symmetrical transition state; this, however, is not at all apparent in the VB description.

Singlet carbene has an empty 2p AO and a filled hybrid AO. The former can be used as an acceptor in forming a π bond to ethylene and the latter as donor for back-coordination. Since, however, the filled AO is not symmetrical, the best orbital overlap will no longer correspond to a situation where the carbene carbon lies on the perpendicular bisector of the C=C bond. The resulting π complex will therefore have a skew structure (Figures 5i,j), accounting for the unsymmetrical approach of singlet carbene to ethylene.

This argument can be extended to chelotropic reactions. A typical chelotropic reagent is one in which the central atom has a filled hybrid AO and an empty p AO, these being used to form the two new bonds to the polyene substrate. In the preferred mode of approach, the filled hybrid AO interacts in σ fashion with the terminal 2p AO's of the polyene, while the empty p AO interacts in π fashion, for example:



If the resulting transition state is aromatic, i.e., if the reaction is "allowed", then the interactions will be bonding with both ends of the polyene. The transition state should then be symmetrical, the interactions in it being precisely analogous to those in an olefin–O_2 π complex. It is, however, possible in principle for a chelotropic reaction to take place by an alternative "allowed" path in which the p AO of the reagent is used for σ-type bonding and the hybrid AO for π-type bonding. In that case the transition state will be unsymmetrical, like that for addition of singlet carbene to ethylene and for the same reason.

Conclusions

Previous applications of MINDO/3 to organic reactions have been mainly concerned with cases when the mechanisms were known, or thought to be known. The primary purpose was as much to test MINDO/3 as to obtain mechanistic information, although in fact our calculations led to a number of surprising conclusions which were either subsequently confirmed by experiment or could be shown to account for experimental results that had been largely ignored.[73] Here we have studied a reaction where no mechanism has been definitely established in the hope of providing information that cannot easily be derived from experiment.

The results of our calculations seem indeed to lead to a unifying mechanistic scheme for the reactions of $^1\Delta_g\ O_2$ with olefins which is consistent with all the available experimental evidence. It seems that none of these reactions are concerted. The reaction of $^1\Delta_g\ O_2$ with olefins invariably leads initially to an intermediate peroxirane or zwitterion which subsequently rearranges to the observed product or products. In view of the very extensive tests to which MINDO/3 has by now been subjected and which it has survived, we feel that this prediction is a very strong one and can certainly be accepted as a working basis by organic chemists. It is true that the energies we calculate are subject to error, given the large difference (14 kcal/mol) between the calculated and observed heats of formation of oxirane; however, such an error would not invalidate our conclusions.

These results, and studies of numerous other reactions, seem to suggest that MINDO/3 can provide information concerning the mechanisms of reactions which is at least as reliable as that available from current experimental techniques. Our theoretical approach has the further advantage of providing detailed information concerning the geometries and other properties of transition states, information which can be inferred from experiment only very indirectly and with much uncertainty. While better semiempirical procedures will undoubtedly be developed, MINDO/3 already seems to be sufficiently accurate and reliable to serve as a useful chemical tool.

References and Notes

(1) Part XXIX: M. J. S. Dewar, D. H. Lo, and C.A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1311 (1975).
(2) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
(3) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3880 (1964).
(4) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965).
(5) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(6) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).
(7) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); *Adv. Chem. Ser.*, **77**, 78 (1968).
(8) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).
(9) C. S. Foote, *Pure Appl. Chem.*, **27**, 635 (1971).
(10) R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).
(11) D. R. Kearns, *J. Am. Chem. Soc.*, **91**, 6554 (1969).
(12) D. R. Kearns, W. Fenical, and P. Radlick, *Ann. N.Y. Acad. Sci.*, **171**, 34 (1970).
(13) K. Yamaguchi, T. Fueno, and H. Fukutome, *Chem. Phys. Lett.*, **22**, 466 (1973).
(14) P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223 (1970).
(15) S. Mazur and C. S. Foote, *J. Am. Chem. Soc.*, **92**, 3225 (1970).
(16) C. S. Foote and J. W. P. Lin, *Tetrahedron Lett.*, 3267 (1968).
(17) N. M. Hasty and D. R. Kearns, *J. Am. Chem. Soc.*, **95**, 3380 (1973).
(18) A. P. Schaap and G. R. Faler, *J. Am. Chem. Soc.*, **95**, 3381 (1973).
(19) S. Inagaki, S. Yamabe, H. Fujimoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 3510 (1972).
(20) A. Nickon and F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961).
(21) D. B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N.Y., Sept 1960, No. 79P.
(22) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965).
(23) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91**, 3396 (1969).
(24) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).
(25) C. S. Foote and R. W. Denny, *J. Am. Chem. Soc.*, **93**, 5162, 5168 (1971).
(26) J. C. Carmier and X. Deglise, *Bull. Soc. Chim. Fr.*, 868 (1973).
(27) L. M. Stephenson, D. E. McClure, and P. K. Sysak, *J. Am. Chem. Soc.*, **95**, 7888 (1973).
(28) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).
(29) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).
(30) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).
(31) N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **94**, 5303 (1972).
(32) A. Brown, M. J. S. Dewar, H. W. Kollmar, D. H. Lo, H. Metiu, P. J. Student, J. S. Wasson, and P. K. Weiner, to be published.
(33) R. Fletcher and M. J. D. Powell, *Computer J.*, **6**, 163 (1963); W. C. Davidon, *ibid.*, **10**, 406 (1968).
(34) J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).
(35) J. W. McIver, Jr., *Acc. Chem. Res.*, **7**, 72 (1974).
(36) A. Komornicki, Ph.D. Thesis, State University of New York, Buffalo, N.Y., Feb 1974.
(37) For the location of the transition states and for the diagonalization of the force constant matrix, we used programs written by A. Komornicki.
(38) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **93**, 4291, 4292 (1971).
(39) M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Am. Chem. Soc.*, **96**, 5242 (1974).
(40) R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9107 (1972).
(41) The largest decrease in energy with inclusion of configuration interaction is that for $^1\Delta_g\ O_2$ (8.9 kcal/mol). In this case, the calculated heat of formation without configuration interaction agrees very closely with experiment. For further discussion, see M. J. S. Dewar, R. C. Haddon, W.-K. Li, W. Thiel, and P. K. Weiner, *J. Am. Chem. Soc.*, in press.
(42) M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **93**, 7201 (1971).
(43) J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, **90**, 1349 (1968).
(44) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).
(45) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 7578 (1974).
(46) E. Koch, *Tetrahedron*, **24**, 6295 (1968).
(47) J. E. Huber, *Tetrahedron Lett.*, 3271 (1968).
(48) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, **171**, 79 (1970).
(49) P. D. Bartlett and M. S. Ho, *J. Am. Chem. Soc.*, **96**, 627 (1974).
(50) An interesting possibility is the reaction of the peroxirane with $^1\Delta_g\ O_2$ to yield the oxirane and ozone. MINDO/3 calculations seem to support its feasibility: M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, to be published.
(51) J. E. Baldwin, A. K. Bhatnagar, S. C. Choi, and T. J. Shortridge, *J. Am. Chem. Soc.*, **93**, 4082 (1971).
(52) F. A. Litt and A. Nickon, *Adv. Chem. Ser.*, **77**, 118–132 (1968).
(53) A. Nickon, V. T. Chuang, P. J. L. Daniels, R. W. Denny, J. B. Di Giorgio, J. Tsunetsugu, H. G. Vilhuber, and E. Werstiuk, *J. Am. Chem. Soc.*, **94**, 5517 (1972).
(54) K. R. Kopecky and J. H. van de Sande, *Can. J. Chem.*, **50**, 4034 (1972).
(55) The good correlation between the relative rates of oxidation and the ionization potential of the olefins[11] provides another indication that the rate-determining step in the ene reaction involves the initial attack of $^1\Delta_g\ O_2$ on the double bond.
(56) A. P. Schaap, *Tetrahedron Lett.*, 1757 (1971).
(57) A. P. Schaap and N. Tontapanisch, *J. Chem. Soc., Chem. Commun.*, 490 (1972).
(58) W. Adam and J. C. Liu, *J. Am. Chem. Soc.*, **94**, 1206 (1972).
(59) W. Ando, J. Suzuki, T. Arai, and T. Migita, *Tetrahedron*, **29**, 1507 (1973).
(60) K. Orito, R. H. Manske, and R. Rodrigo, *J. Am. Chem. Soc.*, **96**, 1944 (1974).
(61) K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).
(62) We are aware of the fact that, in Table 2 of ref 54, the increasing product ratio argues against a side reaction. The increasing product ratio, however, is not consistent with an exclusive reaction via the peroxirane.
(63) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).
(64) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(65) J. W. McIver, *J. Am. Chem. Soc.*, **94**, 4782 (1972).
(66) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 6225 (1974).
(67) **5** is definitely a transition state on the potential surface since the force constant matrix had one negative eigenvalue.
(68) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972), and papers cited there.
(69) Note that the process studied by McIver in this connection was the "forbidden" addition involving intermediates with C_{2v} symmetry.
(70) M. J. S. Dewar, *Bull. Soc., Chim. Fr.*, **18**, C86 (1951).
(71) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965).
(72) M. J. S. Dewar, *Nature (London)*, **176**, 784 (1945); *J. Chem. Soc.*, 406 (1946).
(73) See M. J. S. Dewar, *Chem. Br.*, **11**, 97 (1975).