

THE ADDITION OF $^1\Delta_g$ OXYGEN MOLECULE AND ETHENE TO GIVE DIOXETANE: AN MCSCF STUDY AND CHARACTERIZATION OF SOME PREVIOUSLY PROPOSED PATHWAYS

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ABSTRACT

A preliminary survey of the energy hypersurface for the addition reaction of the singlet oxygen molecule and ethene to give dioxetane has been performed at the MC-SCF level of theory using an active space of six orbitals and a minimal basis set. Four modes of approach have been studied by complete optimization of the geometries followed by diagonalization of the Hessian matrices to characterize the critical points as transition states or higher-order saddle points. None of the approaches examined (*supra-supra*, *supra-antara*, *syn* diradicaloid and peroxirane-like) corresponds to a true transition state: there is a strong indication that the only path left to the system is diradical in nature, presumably in correspondence of a *gauche* geometry of approach.

INTRODUCTION

The mechanism of addition of the singlet oxygen molecule [1] to a double bond has been the subject of many experimental and theoretical investigations [2-5]. This reaction can take place either as a 1,2 addition leading to formation of dioxetane, or as a 1,3 addition ("ene" reaction) if at least one allylic hydrogen is present in the substrate. The various experimental studies suggest three different main hypotheses for the dioxetane formation process: (i) a mechanism involving amphoteric intermediates (1,4 zwitterions or peroxide); (ii) a concerted mechanism; (iii) a charge transfer mechanism. A

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diradical mechanism is generally not considered as a realistic candidate, mainly because the expected loss of configuration is not observed and because dioxetane formation is not affected by the addition of radical inhibitors. Much of the support for one or the other of the mechanisms is based on particular reaction conditions or properties of the substrates, causing some difficulties to the drawing of general conclusions.

Recent theoretical studies on this subject have suggested different mechanisms. Dewar and coworkers [3] concluded, on the basis of their MINDO/3 computations, that the reaction is not concerted and that peroxirane or amphiionic species have a role as intermediates. Harding and Goddard [4], on the basis of GVB-CI calculations, have, on the contrary, supported the role of $\text{CH}_2\text{CH}_2\text{OO}$ diradicals. Although no reaction paths were explicitly studied, the peroxirane intermediate was located at higher energy than the diradical minimum, and the energy of open amphiionic structures was also estimated to be significantly higher. Hotokka et al. [5], in a recent MCSCF and CI study, found the formation of a peroxirane intermediate easier than the formation of a diradical (as a matter of fact only the unfavorable *syn* structure was examined). In both these ab-initio studies only limited geometry optimizations were carried out under symmetry constraints. Although the quality of the computed wavefunction is good in both cases, the limitations on the exploration of the energy surface leave the problem of the pathway actually followed by the system still open: in fact, in the former study only minima (intermediates) were explicitly considered, while in the latter, the use of symmetry constraints and the lack of characterization [6] of the critical points considered leaves some doubt about the nature of true transition states of these structures.

Therefore a preliminary study of some of the qualitative features of the energy hypersurface is desirable. In the present work complete geometry optimizations were used to determine the critical points related to different modes of approach, and subsequently their nature was characterized by diagonalization of the related Hessian matrices. The recent MCSCF study of the ethene dimerization reaction [7], which apart from the obvious differences bears some resemblance to the dioxetane formation reaction, has shown that some modes of approach (*supra-supra*, *syn*) lead to second-order saddle points of no chemical interest and not to true transition states. This preliminary survey is, therefore, encouraged by previous experience and may open the way to a more complete study of the system.

METHOD

The calculations were carried out at the MCSCF level of theory [8]. The active space (in which a complete CI is performed) consists of six active orbitals, chosen on the basis of the orbitals of the two separated subsystems, O_2 and C_2H_4 , which contribute more significantly to bond formation: the π and π^* orbitals of ethene and the two degenerate pairs π_u and π_g of the oxygen

molecule. This "minimal" choice nonetheless allows the description of di-radical species on the same foot as closed shell species, and is appropriate for a qualitative description of the energy hypersurface. Integral and derivative calculations were performed by using the Gaussian 80 and 82 series of programs [9].

Previous studies of two organic reactions [7, 10] carried out at the MCSCF level of theory with minimal and extended basis sets have shown that, although the energetics can be significantly affected by the change of basis set, the qualitative features of the energy hypersurface, such as the nature of the critical points, do not change. This experience suggests that the minimal STO-3G basis set [11] can be an appropriate choice for a preliminary survey to assess the presence of first- or higher-order saddle points on the reaction paths of different symmetries.

The geometries of the critical points were completely optimized at the MCSCF level using gradient methods [12]. The Hessian matrices for these points were computed numerically in the subspace of the coordinates of the non-hydrogen atoms. The critical points can be characterized in terms of the number of negative eigenvalues of the Hessian matrix. Thus a transition state corresponds to a Hessian with one and only one negative eigenvalue, while a Hessian with more than one negative eigenvalue corresponds to saddle points of no chemical significance.

RESULTS AND DISCUSSION

Several modes of approach of O₂ to ethene (described in Fig. 1) have been investigated by the computational procedure outlined above. The energies and energy differences of the corresponding critical points, relative to the dissociation limit, are reported in Table 1. The detailed geometries will be published elsewhere; here the accent is on the nature of these critical points, as determined by diagonalization of the relevant Hessian matrices.

The directions of negative curvature of the energy hypersurface other than the one dominated by the separation (or approach) of the two moieties are approximately indicated in Fig. 1, with arrows corresponding to the internal coordinates dominating the relevant eigenvectors.

Two of the approaches are concerted and synchronous [13]: (a) the "supra-supra" approach, of C_{2v} symmetry; and (b) the "supra-antara" approach, of C₂ symmetry, in which the O₂ molecule is involved *antara*-facially, as suggested by Bartlett [14]. Other paths include (c) the *syn* di-radicaloid approach, of C_s symmetry, representative of an asynchronous but possibly still concerted mechanism; and (d) an attack of C_s symmetry leading directly to the peroxirane intermediate.

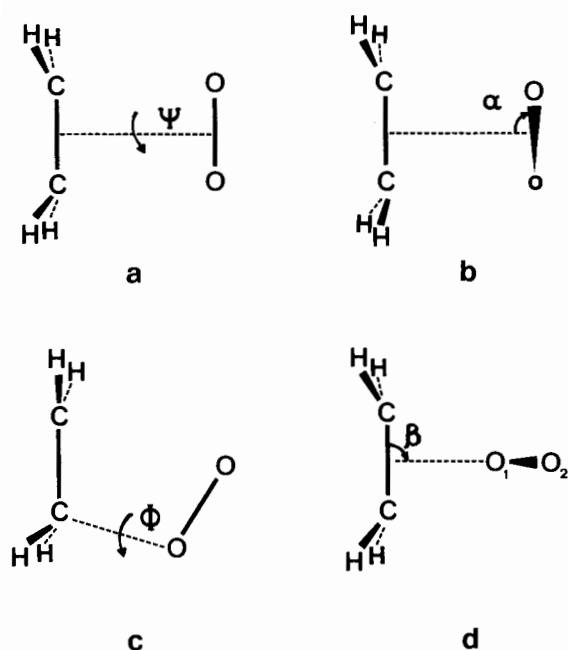


Fig. 1. Modes of approach of O_2 to ethene: (a) *supra-supra*, C_{2v} symmetry; (b) *supra-antara*, C_2 symmetry; (c) *syn* diradical, C_s symmetry; (d) attack of C_s symmetry leading to peroxirane intermediate.

(a) Supra-supra approach

In this approach only one π system of O_2 is directly engaged in the bond formation process; the approach is symmetry forbidden [5] as the analogous *supra-supra* attack in the dimerization of ethene [7]. The critical point found is located 53 kcal mol^{-1} above the dissociation limit (see Table 1). The Hessian matrix has two negative eigenvalues: the first in connection with an eigenvector dominated by R , the distance between the two midpoints of the CC and OO bonds; the second related to ψ , the torsional angle around the C_2

TABLE 1

Energies and energy differences of corresponding critical points

	Energies (Hartree)	Energy differences (kcal mol^{-1})
Dissociation limit	-224.774 311	0.00
<i>Supra-supra</i>	-224.690 755	52.54
<i>Supra-antara</i>	-224.691 941	51.69
<i>Syn</i> diradicaloid	-224.726 466	30.02
Peroxirane-like	-224.673 727	63.12

axis (Fig. 1a). In this second direction, the surface is flatter than in the first. This critical point is, therefore, classified as a second-order saddle point, i.e., a maximum in two coordinates, similar to the ethene dimerization [7] (but there the second direction of negative curvature was an in-plane opening of the CCCC skeleton). The instability with respect to a torsion around the C_2 axis suggests the possibility of finding a C_2 critical point related to it by relaxing the geometry along this direction.

(b) *Supra-antara approach*

This attack involves both π systems of O_2 in the interaction with the π system of C_2H_4 . Preliminary single-point computations cutting the surface in function of the torsional angle ψ , have shown the existence of a well defined minimum around $\psi = 15^\circ$ with the energy raising sharply for ψ larger than 30° . The full optimization yields a critical point with an energy only slightly lower than that of the *supra-supra* point (see Table 1). A distance of 2.02 Å between the two moieties was found, close to the value of 2.03 Å found in the *supra-supra* case, with a torsional angle of 23° . The nature of the *supra-antara* critical point is again that of a second-order saddle point. Of the two negative eigenvalues, the lowest is associated with an eigenvector dominated by R , as in the *supra-supra* case, the second with a planar angle, α , which is defined by the two midpoints of the CC and OO bonds and one oxygen atom (Fig. 1b). Relaxing the geometry along this degree of freedom would lead to a C_1 (*gauche*) species of diradical character. In the case of the dimerization of ethene [7], the *supra-antara* critical point was found to be a transition state (first-order saddle point); but it was located at a much higher energy than the *supra-supra* critical point, due to the torsional deformation required in the ethene molecule attacking *antarafacially*.

(c) *Syn diradicaloid approach*

If this approach were to lead to a true transition state, the reaction would presumably be an asynchronous but concerted (one-step) one. But, as discussed by Harding and Goddard [4], a coplanar approach is unfavourable to immediate closure of the ring, because of the occupancy of the p orbitals in the peroxy diradical. A rotation along the C—O bond is necessary to develop a bonding situation between the two terminal radical lobes. Full optimization gives a critical point located 30 kcal mol⁻¹ above the dissociation limit with a C—O distance (1.84 Å) which is shorter than in the *supra-supra* and *supra-antara* approaches. As expected, this is a second-order saddle point, one of the two directions of negative curvature being along a coordinate dominated by the shorter C—O distance, the other along the torsional angle CCOO (ϕ in Fig. 1c). The surface is very flat in the latter degree of freedom. A deformation along this dihedral angle would bring again to a C_1 (*gauche*) structure. Therefore another possibility of concerted approach, having this

time diradical character, is to be ruled out. On the other hand, if a diradical path exists, it does not pass through a structure of this symmetry. Nevertheless, the energy of the C_s critical point, 30 kcal mol⁻¹, is an upper bound to the activation energy for the diradical pathway at this level of computation.

(d) *Peroxirane-like attack*

A peroxide has often been invoked as an intermediate [3, 14] to explain experimental findings, or postulated as a possible "quasi-intermediate" [15]. If peroxirane is a minimum on the energy hypersurface, it is rather important to determine if it can be reached directly via an approach of the same symmetry (C_s). A critical point of C_s symmetry was found, located 63 kcal mol⁻¹ above the dissociation limit, at a C—O₁ distance of 1.67 Å (Fig. 1d). The Hessian matrix again has two negative eigenvalues, and this structure is unstable, not only with respect to the distance between the midpoint of the CC bond and the closest oxygen atom, but also with respect to an opening of the planar angle β (Fig. 1d), i.e., in a direction leading again toward a C_1 structure of diradical character. It appears, therefore, that this last kind of diradical approach is the only one left to provide a pathway from the two separated molecules not only to dioxetane, but possibly also to peroxirane.

CONCLUSIONS

The aim of this preliminary MCSCF study of the energy hypersurface for the addition of ethene and ¹ Δ_g oxygen molecule has been to obtain a qualitative description of its shape in correspondence to some modes of approach traditionally considered as possible candidates for mechanisms. For all of these approaches (the C_{2v} *supra-supra*, the C_2 *supra-antara*, the C_s *syn* diradicaloid and the C_s peroxirane-like attack), critical points were found on the surface. Diagonalization of the relevant Hessian matrices in the subspace of the coordinates of the heavier atoms indicates that all of these are higher-order saddle points and not transition states. The information provided by the Hessian matrices suggests that a pathway of chemical interest for the system may correspond to a transition state of diradical nature with a geometric structure different from the one studied here (*syn*). The natural extension of this preliminary study is the exploration of the *gauche* and *anti* diradical pathways and subsequently the re-examination of the whole surface with an extended basis set to obtain better energetics.

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