References and Notes

(1) Research carried out at Brookhaven National Laboratory under contract with the U.S. Energy Research and Development Administration.

(2) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *J. Am. Chem. Soc.*, **88**, 5525 (1966).

(3) S. I. Miller, *Adv. Phys. Org. Chem.*, **6**, 185 (1968).

(4) O. S. Tee, *J. Am. Chem. Soc.*, **91**, 7144 (1969).

(5) O. S. Tee and K. Yates, *J. Am. Chem. Soc.*, **94**, 3074 (1972).

(6) S. Ehrenson, "Chemical and Biochemical Reactivity", Proceedings of the International Jerusalem Symposium, 6th, 1974, pp 113–130.

(7) S. Ehrenson, *J. Am. Chem. Soc.*, **96**, 3778 (1974).

(8) S. Ehrenson, *J. Am. Chem. Soc.*, **96**, 3784 (1974).

(9) N. B. Slater, "The Theory of Unimolecular Reactions", Cornell University Press, Ithaca, N.Y., 1959; *Proc. R. Soc.* (*London*), *Ser. A*, **194**, 112 (1948).

(10) R. D. Finney and G. G. Hall, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 489 (1970).

(11) One may rather easily show that the same overall (whole molecule) center-of-gravity conditions are required for transformation to this new fragment coordinate system from arbitrary positioning of the initial and final species and that appropriate rotation by the angle γ will accomplish rotational optimization where both states share a plane of symmetry (have at least C_s symmetry), where

$$\tan\gamma = \frac{\sum_{i=1}^{N} \mu_i(\bar{q}_i\bar{p}_i' \mp \bar{p}_i\bar{q}_i') + \sum_{K=1}^{2} M_K(\bar{Y}_K\bar{X}_{K'} \mp \bar{X}_K\bar{Y}_{K'})}{\sum_{i=1}^{N} \mu_i(\bar{q}_i\bar{q}_i' \pm \bar{p}_i\bar{p}_i') + \sum_{K=1}^{2} M_K(\bar{Y}_K\bar{Y}_{K'} \pm \bar{X}_K\bar{X}_{K'})}$$

The barred coordinates are those which are obtained following the whole-molecule CG (translational) transformations.

(12) See, e.g., G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1945, pp 142–147.

(13) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955, pp 28–31.

(14) For $C_{18}H_{38}$, $m = 1.993 \times 10^{-23}$ g, a_c, the critical coordinate extension, one equilibrium bond length (a_e, which is 1.55×10^{-8} cm), and the force constant $mk^2 = 5 \times 10^5$ erg cm^{-2}. The minimum degree of excitation accompanying ionization, n, is 6, obtained as for a pseudodiatomic from $\Delta E = nh\nu$, where ΔE is the difference in vertical and photoionization potentials, extrapolated from known values for smaller hydrocarbons, and ν is the frequency of the C–C alkane bond; $\hbar = 1.054 \times 10^{-27}$ erg s. Note, of course, that *n*-alkanes while "linear" chains are not one-dimensional vibrators but have bending modes. They are the closest real molecule analogues to the models, however. Likewise, it should be apparent that *temporal* correlation of favorable local break with unfavorable CG motions, and vice versa, cannot be made with these models which employ expectation values of critical coordinate functions.

(15) The figures given in parentheses are the $-\log P$ (or $-\log \mathcal{P}$) values for the central bond. While the absolute values of these numbers have little meaning because other factors on the rate such as collision frequencies have not been considered, their relative values should, and the large numbers obtained for the molecule with both ends bound suggests a very improbable process.

(16) F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, New York, N.Y., 1957.

(17) See, for example, H.-D. Beckey, "Field Ionization Mass Spectroscopy", Pergamon Press, New York, N.Y., 1971, pp 306–308.

(18) J. E. Germain, "Catalytic Conversion of Hydrocarbons", Academic Press, New York, N.Y., 1969, Chapter 4.

(19) A. Van Hook and P. H. Emmett, *J. Am. Chem. Soc.*, **85**, 697 (1963).

(20) Excitation to a lower n than 6 is probably called for here, the process being much gentler than electron impact ionization. Examination of the relative probabilities for lower n reveals almost identical patterns. E.g., for $n = 2$, with the exception of some minor curvatures at the extremes, the probability functions appear identical but require scaling by $\sim$0.8. Hence the previous conclusions require no modification.

(21) R. H. Schuler and R. W. Fessenden, Proceedings of the Third International Congress on Radiation Research, Cortina, Italy, 1966: see also, R. A. Holroyd, "Fundamental Processes in Radiation Chemistry", Interscience, New York, N.Y., 1968, p 461.

(22) See, e.g., L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics", McGraw-Hill, New York, N.Y., 1935, Chapter 6, Section 23.

(23) J. W. Strutt (Baron Rayleigh), "The Theory of Sound", Vol. 1, Dover Publications, New York, N.Y., 1945, Chapter 4, Section 90.

(24) M. Wolfsberg, *J. Chem. Phys.*, **33**, 21 (1960).

(25) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, 1960, p 231.

Mechanism of Ozonolysis. Ab Initio Study of the Primary Ozonide and Its Cleavage to the Criegee Intermediate

Philippe C. Hiberty

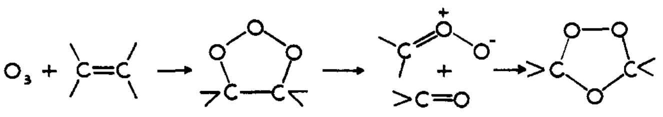
Contribution from the Laboratoire de Chimie Théorique,[1] *Université de Paris-Sud, 91405 Orsay, France.*

Received September 26, 1975

Abstract: Part of the ozonolysis reaction has been investigated by means of an ab initio SCF MO theory. Several possible primary ozonides have been tested and the 1,2,3-trioxolane, with an O-envelope conformation, is retained as being slightly more stable than the C–C half-chair and planar forms. Two state correlation diagrams show that the planar cleavage is thermally forbidden and that the envelope 1,2,3-trioxolane can collapse, by a symmetry allowed 1,3 dipolar cycloreversion, to the Criegee zwitterion. The activation energy of this process has been estimated by a CI calculation and is consistent with the instability of the primary ozonide.

I. Introduction

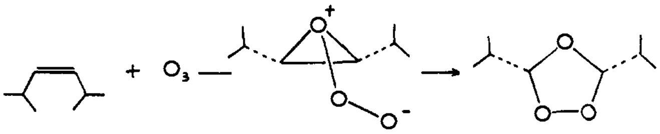
The mechanism of the ozonolysis of olefins, both in liquid and gaseous phase, has been a subject of wide interest. Many proposals have been put forward, but all of them involve a more or less modified Criegee[2] mechanism, at least as a competing pathway. In its original form, it is simply suggested that the ozone molecule adds to the olefin to form a 1,2,3-trioxolane ring (**1**), which cleaves to give a zwitterionic methylene peroxide and an aldehyde. These two products react further to give the final ozonide (**2**). But some facts are not explained by this simple scheme; in particular, it is known that the cis/trans ratio of the final cross ozonide depends on olefin geometry.[3] This led Story, Murray, and Youssefyeh to propose a so-called "aldehyde interchange" mechanism,[4] in which an aldehyde can be incorporated in the 1,2,3-trioxolane ring. In addition, they suggest a more direct pathway for sterically hindered cis olefins, via the σ complex (**3**), to account for the high cis/trans ozonide ratio[4] obtained with bulky cis olefins, as well as the high yields of ozonides.[3a,b] On the other hand, Bauld, Bailey, and co-workers proposed a revised version of the Criegee



1

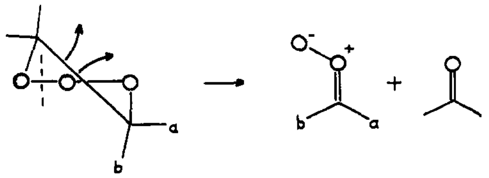
polyperoxide
hydroperoxide

2



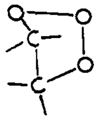
3

mechanism.[5] Assuming a C–C half-chair conformation for the 1,2,3-trioxolane, they suggested a disrotatory cleavage of this molozonide to give a carbonyl compound and a syn or anti zwitterionic carbonyl oxide:



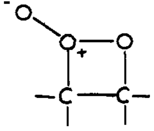
The final ozonide was assumed to have a C–O half-chair conformation, and three rules were stated concerning the stereochemistry of the reaction. Later,[6] some of these rules were modified to account for the observed conformation of the final ozonide (O–O half-chair instead of C–O half-chair), for reactions with ethylene,[7] propylene, and *trans*-2-butene.[6]

Experiments have been realized in the presence of ^{18}O-labeled aldehyde to test the relative importance of the aldehyde interchange mechanism and the Bauld–Bailey mechanism. The former predicts that ^{18}O can be incorporated only at the peroxidic site of the final ozonide, while the latter is coherent with ^{18}O only at the ether site. The results seem to depend on the olefin. In some cases, ^{18}O has been detected in the peroxidic bridge,[8,10–14] while it is present only at the ether site in a number of other cases.[15–19] The original Bauld-Bailey mechanism was consistent with the cis/trans ratio of ozonides obtained from bulky olefins but inadequate for reactions with small olefins. This, together with the new data concerning the final ozonide conformation, led Lattimer et al. to propose two revisions of the Bauld-Bailey rules, which are abundantly discussed in a recent paper.[6b] The major assumption (first "rule") remains that there is a disrotatory cleavage of the 1,2,3-trioxolane ring in its C–C half-chair conformation. But this geometry has never been experimentally determined, due to the great instability of the primary ozonide, and is supported only by extended Hückel calculations.[20] Moreover, the adequacy of the EHT method for heterocycles with adjacent heteroatoms has been criticized by Rouse.[21] On the other hand, the cleavage of the primary ozonide can be considered a 1,3 cycloreversion, the reverse of a $_{\pi}4_s + _{\pi}2_s$ addition. The orbital correlation diagram of a similar system[22] (allyl anion reacting with ethylene) shows that this reaction should be symmetry allowed. According then to the view of Lattimer et al., the transition state is likely to resemble an exaggerated envelope (**4**). This reaction process involves a nonrotatory cleavage, and the steric constraints on the transition state differ from that suggested by Bauld and Bailey. The stereochemical consequences of this mechanistic scheme have been discussed in detail.[6b]



4

An additional intermediate, the Staudinger molozonide (**5**), has also been proposed.[23–25] This four-membered ring, formed via **3** or directly through a 1,2 cycloaddition of ozone to the olefin, is assumed to collapse to the 1,2,3-trioxolane, or to cleave to the Criegee zwitterion, or even to rearrange intramolecularly to the final ozonide.[25] This interpretation has been contested by Bailey[26] et al. Finally, to account for the chemiluminescence and the radical intermediates observed in gas phase,[27–29] one must add the O'Neal and Blumstein mechanism,[30] which rationalizes the experimental data in terms of α-H and β-H abstraction from the primary diradical formed by breaking the O–O bond of the 1,2,3-trioxolane. This competing series of reactions is discussed in a recent paper.[29]



5

The aim of the present work is, on the one hand, to rule out some of the proposed intermediates for the ozonolysis reaction and, on the other hand, to support a concerted nonrotatory cleavage of the primary ozonide, as suggested by Lattimer et al.,[6b] without ruling out the O'Neal and Blumstein mechanism nor a nonconcerted cleavage as competing pathways. Two reaction paths have been calculated, corresponding respectively to the cleavage of a planar primary ozonide and to that of its envelope conformer. The calculations are ab initio and use the GAUSSIAN 70 series of programs.[31,32] A minimal STO-3G basis set[32a] has been used for the geometry optimizations, and the relative energies of the various molecules taking part in the reaction have been calculated with the 4-31 G basis set.[32b] In all calculations, a limited configuration interaction (CI) has been performed, to take into account the correlation of π electrons.

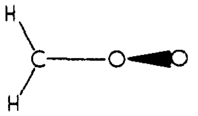
II. Relative Energies of the Products, Intermediates, and Reactants

A. Ozone. Ozone has already been described by Goddard et al.[33] with a GVB method, and by Grimbert[34] with an ab initio Hartree–Fock calculation using Stevens' program.[35] In our calculation, we used the equilibrium geometry optimized by Grimbert[34] at the closed shell SCF stage (r = 1.298 Å and θ = 117°). A limited configuration interaction, involving both single and double excitations from the π nonbonding to the π^* antibonding orbital, was performed to take into account the correlation of π electrons. This limited CI includes the most important configurations necessary to describe the ground state of ozone, as shown by the larger CI calculation of Grimbert.[34] The energy obtained, calculated in the extended basis set (4-31G energy), is −223.971 66 hartrees.

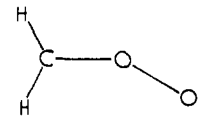
B. Ethylene. The energy of ethylene has already been calculated in a previous work,[36] with a 3 × 3 CI involving the doubly occupied $(\pi, \pi^*)^2$ configuration. The geometry, optimized within this procedure, was r = 1.341 Å and ∠HCH = 116.2°, and the ground state 4-31G energy is −77.945 03 hartrees.

C. Formaldehyde. The 3 × 3 CI used for ethylene has been applied to H_2CO. Similarly, the ground state configuration is mixed with the doubly excited $(\pi, \pi^*)^2$ configuration. We took a standard geometry, r = 1.22 Å and ∠HCH = 120°. The ground state 4-31G energy is −113.722 12 hartrees.

D. Methylene Peroxide. Both perpendicular (**6**) and planar (**7**) methylene peroxide have already been calculated by Goddard[37] with an ab initio GVB method. Our own Hartree–Fock calculations, carried out to obtain relative energies comparable with the other products, are in good agreement with Goddard's calculations. In particular the symmetries of the states are the same with both methods.



6



7

As for ozone, the calculated ground configuration of planar methylene peroxide is a singlet. The ordering of frontier orbitals is shown in Figure 1a. A 6 × 6 CI, involving the two highest occupied and the lowest unoccupied molecular orbitals, has been necessary to describe properly the first excited state.

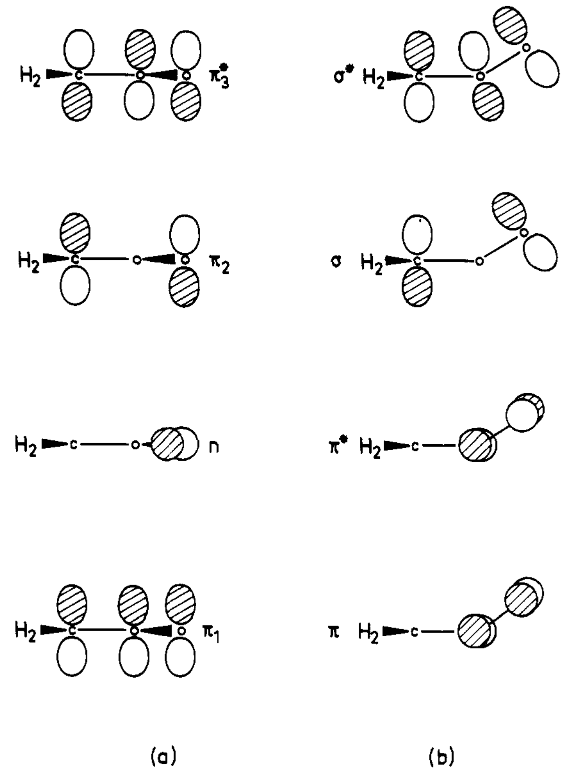
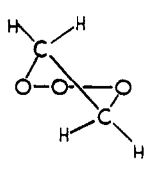


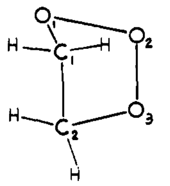
Figure 1. Molecular orbitals of the planar methylene peroxide (a) and the perpendicular methylene peroxide (b).

The result is a ($^1A'$, 4π) ground state having as major components the ground configuration (n^2, π^2) mixed with the doubly excited (π_2, $\pi_3{}^*)^2$ configuration and, to a lesser extent, the singly excited (π_2, $\pi_3{}^*$) configuration. The geometry optimization gave the following values: r_{CO} = 1.367 Å, r_{OO} = 1.269 Å, ∠COO = 117.5°, 4-31G energy = −188.271 81 hartrees. The ∠HCO angles were fixed at 120°. The first excited state, in our calculations, is of ($^1A''$, 5π) type and is described by two configurations: the singly excited (n, $\pi_3{}^*$) and the doubly excited (n, $\pi_3{}^*$)(π_2, $\pi_3{}^*$). Although we think that the (4π) ground state is sufficiently well described by our limited CI, we realize that the first excited state could be improved by a larger CI and the use of diffuse orbitals and that the 2.64 eV gap between these states could be reduced. Nevertheless, contrary to the ground state, the first excited state need not be calculated accurately since we use it solely to plot a qualitative state correlation diagram. The same 6 × 6 CI has been applied to the perpendicular conformer (see the ordering of frontier orbitals in Figure 1b); its ground state is essentially described by the open shell component (π^*, σ^*), mixed with the doubly excited (π^*, σ^*)(σ, σ^*) one. This is a ($^1A''$, 3π) state, while the first excited state is ($^1A'$, 4π), involving mainly the ground configuration mixed with the (σ, σ^*) and (σ, $\sigma^*)^2$ configurations, and lying 1.56 eV above the 3π ground state. The geometry optimization of this ground state gave the following parameters: r_{CO} = 1.433 Å, r_{OO} = 1.269 Å, ∠COO = 117.2°, ∠HCO being chosen equal to 120°. Due to the lack of resonance in the π system, the perpendicular methylene peroxide is less stable than its planar conformer by 12.4 kc/mol, with a 4-31G energy of −188.251 99 hartrees. This energy has been obtained with Nesbet's restricted open shell procedure,[38] which gives a better value than the closed shell method for this molecule.

E. 1,2,3-Trioxolane. We optimized the geometry of two conformations: C-C half-chair (**8**) and oxygen (adjacent to carbon) envelope (**9**). For these calculations, no CI was necessary since it concerned saturated compounds.



8



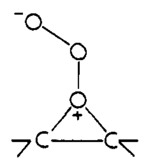
9

(a) **C-C Half-Chair Conformation** (**8**). This is the conformation assumed by Bauld, Bailey, et al.[5] to support their reaction scheme. We optimized five parameters, and the remaining ones were fixed as follows: r_{CH} = 1.09 Å, ∠HCO = 109°, ∠HCC = 109°. The C_2 symmetry has been kept in the optimization procedure. We found the following equilibrium geometry: r_{CC} = 1.543 Å, r_{CO} = 1.442 Å, r_{OO} = 1.419 Å, ∠OOO = 109.3°. Lastly, the angle between the C-C axis and the OOO plane is 19.0°.

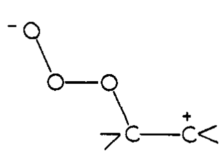
(b) **Envelope Conformation** (**9**). This conformation is suggested by Lattimer et al.[6b] in their orbital symmetry analysis. As in the previous geometry optimization, we chose r_{CH} = 1.09 Å, ∠HCO = 109°, ∠HCC = 109°, $r_{C_1C_2}$ = 1.543 Å. All the remaining parameters were optimized and have the following values: $r_{O_2O_3}$ = 1.419 Å, $r_{C_2O_3}$ = 1.451 Å, $r_{O_2O_1}$ = 1.408 Å, $r_{C_1O_1}$ =1.447 Å, $\angle C_1C_2O_3$ = 104.9°, $\angle O_2O_3C_2$ = 107.3°, puckering angle[39] = 142.9°. Table I shows that this conformation is slightly more stable than the previous one, which argues in favor of Lattimer's suggestion.

(c) **Planar Conformation.** We did not carry out the full geometry optimization of this conformer, since it is not involved in the best reaction process, as shown by the state correlation diagram (Figure 2). Therefore, we simply took, for the planar form, the geometry of the envelope form with a zero-puckering angle. The ground state energy of this conformer is shown in Table I.

F. Other Possible Conformations of the Primary Ozonide. These conformers involve a four-membered ring (**5**), a three-membered ring (**10**), and an open complex (**11**). Although they are not supported unambiguously by any experiment, we made a rough calculation of their ground state energies. Because of the abnormal conformations of these compounds, the convergence to the SCF wave functions was not easy to obtain, and therefore we contented ourselves with STO-3G energies and reasonable geometries, without optimization. A 3 × 3 CI, involving the highest occupied and lowest unoccupied molecular orbitals, was performed in the case of the open complex (**11**), to account for its strong diradical character, due to the presence of a trivalent carbon and a monovalent oxygen. This is not true, of course for **5** and **10** and for these conformers the CI was not judged necessary. We chose r_{CC} = 1.56 Å, r_{CO} = 1.43 Å, r_{O^+O} = 1.50 Å, $r_{O^+O^-}$ = 1.37 Å, r_{CH} = 1.09 Å, ∠HCC = ∠HCO = 117.5° for structure **5**; r_{CC} = 1.50 Å, r_{CO^+} = 1.615 Å, r_{O^+O} = 1.48 Å, r_{OO^-} = 1.32 Å, r_{CH} = 1.09 Å, ∠HCC = 119.8°, ∠HCO = 110.4° for structure **10**; r_{CC^+} = 1.50 Å, r_{CO} = 1.43 Å, r_{OO} = 1.42 Å, r_{OO^-} = 1.269 Å, r_{CH} = 1.09 Å, r_{C^+H} = 1.09 Å, $\angle O^-OO$ = 117.5°, ∠OOC = 108°, $\angle OCC^+ = \angle HCC^+$ = ∠HCO = 109.5°, $\angle HC^+C$ = 120° for structure **11**. Although no firm conclusion can be based only upon STO-3G energies, Table I suggests that these conformers are unlikely to be possible intermediates in the route to ozonide, having ground state energies far above that of both the 1,2,3-trioxolane and the olefin + ozone system.



10



11

Table I. Calculated Ground State Relative Energies of the Possible Primary Adducts of Ozonolysis, with Respect to the Reactants[a]

Compound	Energy STO-3G, kcal/mol (hartrees)	Energy 4-31G, kcal/mol (hartrees)
Ozone + ethylene	0 (−298.507 29)	0 (−301.916 69)
Half-chair 1,2,3-trioxolane	−53.5 (−298.592 61)	−39.7 (−301.980 02)
Envelope 1,2,3-trioxolane	−56.3 (−298.597 07)	−40.7 (−301.981 54)
Planar 1,2,3-trioxolane	−52.0 (−298.590 18)	−34.8 (−301.972 16)
Four-membered ring (**5**)	67.1 (−298.400 35)	
Three-membered ring (**10**)	104.5 (−298.340 79)	
Open complex (**11**)	56.0 (−298.418 21)	

[a] Relative energies are in kcal/mol. In parentheses are reported the total energies in hartrees.

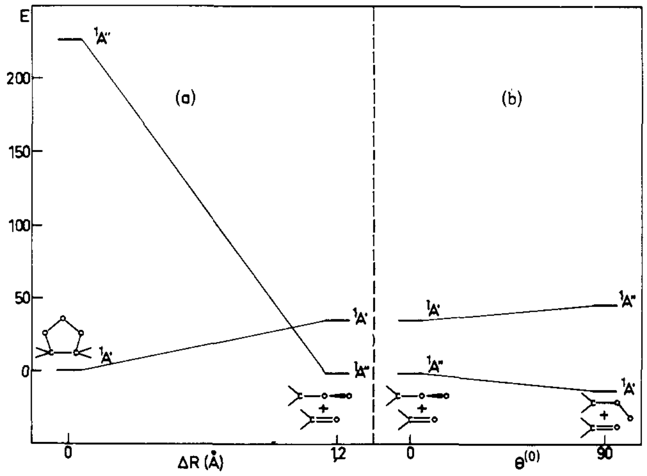


Figure 2. (a) State correlation diagram for the cleavage of the planar methylene peroxide to the perpendicular methylene peroxide (reaction coordinate = ΔR). (b) Rotation of the planar methylene peroxide to its planar conformer (reaction coordinate = θ). Energies are in kcal/mol and are calculated in the 4-31G basis set.

III. Cleavage of the Primary Ozonide

In a first step we considered a simplified two-step reaction process, where first the planar primary ozonide cleaves and collapses to an aldehyde and a perpendicular methylene peroxide, and second this diradical rotates to its planar conformer. Next we calculated a more realistic one-step pathway, where the envelope primary ozonide cleaves directly to the planar methylene peroxide. In both cases a concerted cleavage of the primary ozonide has been assumed, and the reaction coordinate R is defined as follows: R is the distance from C_2 to the C_1O_2. For the rotation of methylene peroxide, θ is the twisting angle of the CH_2 group; $\theta = 0°$ for the perpendicular form and 90° for the planar form.

A. Cleavage of the Planar Primary Ozonide. We kept the plane of the 1,2,3-trioxolane molecule as plane of symmetry throughout the reaction path. The HOMO (π type) and LUMO (σ type) of the primary ozonide are antisymmetric and symmetric, respectively, relatively to this symmetry plane. The ground state has the $^1A'$ symmetry, and the first excited singlet state, which involves exclusively the singly excited configuration (HOMO, LUMO), has the $^1A''$ symmetry. Since the ordering of singlet states in the perpendicular methylene peroxide is precisely the opposite, there must be a surface crossing[40] between the two singlets along the reaction coordinate. This is shown schematically in Figure 2. We may conclude that this pathway, if it occurs, must lead to excited products (perpendicular or planar excited methylene peroxide). However, $H_2\dot{C}O\dot{O}$ has not been identified as a chemiluminescing species.[41] This is not surprising since the system formed with the $^1A'$ state of the perpendicular methylene peroxide and the formaldehyde lies 34.7 kcal/mol above the planar trioxolane, which is itself less stable than its envelope conformer by 5.9 kcal/mol. On the other hand, a cleavage to the $^1A''$ state of the perpendicular methylene peroxide, which could then rotate to its planar form, would necessitate an internal conversion.

Table II. Optimized Parameters of the Intermediate Points in the Symmetry Allowed 1,3 Dipolar Cycloreversion

ΔR, Å	0.3	0.6	0.9	1.2
$r_{C_2O_3}$, Å	1.419	1.308	1.238	1.226
$r_{C_1O_1}$, Å			1.382	
$r_{O_1O_2}$, Å			1.288	
$\angle C_1C_2O_3$, deg			100.3	
$\angle O_2O_3C_2$, deg			104.5	
Puckering, deg	50.4		71.2	
$\angle H_1C_1C_2$, deg	103.4		89.8	
$\angle H_2C_1C_2$, deg	105.5		112.4	

B. Cleavage of the Envelope Form of the Primary Ozonide. This cleavage leads directly to the coplanar methylene peroxide via a strongly bent envelope-looking transition state. Between the initial 1,2,3-trioxolane and the planar methylene peroxide + aldehyde system, we calculated four intermediate points, corresponding to the values 0.3, 0.6, 0.9, and 1.2 Å for ΔR. We optimized the C_2–O_3 bond length for each point and the most important remaining parameters for the first and third points, corresponding to $\Delta R = 0.3$ and 0.9 Å, respectively (see Table II). The nonoptimized parameters have been deduced by extrapolation. As expected, since no symmetry element exists throughout the reaction, our STO-3G curve exhibits no state crossing. To estimate the activation energy corresponding to this process, we calculated the four previous intermediate points in 4-31G basis set. Unfortunately, the number of atomic orbitals is too large, with this basis set, to allow a large CI calculation with our program. Only a limited 3 × 3 CI, involving the HOMO and the LUMO, was possible. The corresponding energy curve is shown in Figure 3, and the calculated activation energy is 33.1 kcal/mol. This value is, of course, exaggerated by the lack of CI. To evaluate the stabilization brought by a more accurate description, we recalculated this potential curve, in STO-3G, with both a 3 × 3 CI and a larger CI taking into account the correlation of the π electrons of formaldehyde and the σ electrons of the breaking O–O and C–C bonds and describing correctly the twisted methylene peroxide. From these calculations one can deduce the stabilization brought by the large CI with respect to the 3 × 3 CI. Assuming the stabilization due to the additional CI not to depend too strongly on the basis set, we can carry it over from curve I and obtain the more realistic curve II. Then the activation energy is reduced to 11 kcal/mol, which could account for the great instability of the primary ozonide.[42] The transition state corresponds to $\Delta R = 0.6$ Å, and its geometry can be deduced from Table II. In particular, the puckering angle is 60.8°, which supports the model of an exaggerated envelope conformation of the transition state and its stereochemical consequences.

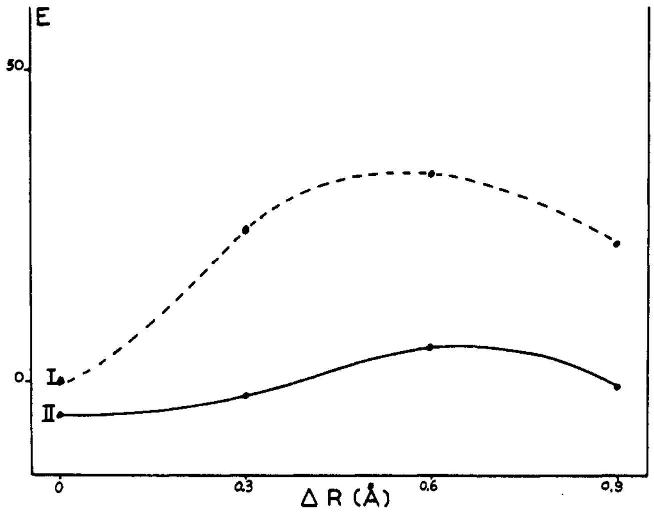


Figure 3. Ground state potential curves, in kcal/mol, of the symmetry allowed 1,3 cycloreversion, calculated in the 4-31G basis set. Dotted lines correspond to energies calculated with 3 × 3 CI, and full lines correspond to the estimated large CI energies.

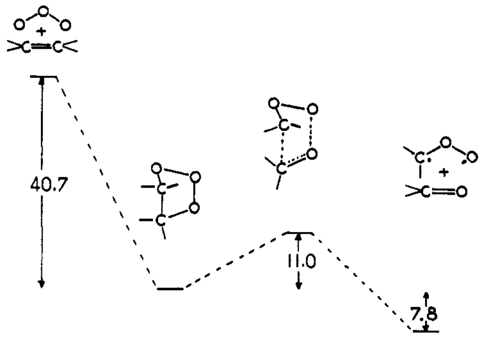


Figure 4. Relative calculated 4-31G energies, in kcal/mol, of the ozone + olefin system, the O-envelope 1,2,3-trioxolane, the transition state, and the planar methylene peroxide + formaldehyde system.

The relative energies of the ozone + olefin system, the O-envelope 1,2,3-trioxolane, the transition state, and the formaldehyde + planar methylene peroxide system, calculated with the extended basis set, are shown in Figure 4.

IV. Conclusion

These results suggest that the ozonolysis reaction does not occur via intermediates of type **5**, **10**, and **11**. The initial adduct is a 1,2,3-trioxolane, and its planar cleavage to a perpendicular methylene peroxide would lead to excited products. Emission of such products, however, has not been observed. Lattimer's suggestion of an envelope-looking transition state is supported by a favorable state correlation diagram, the conformation of our calculated transition state, the low activation energy corresponding to this process, and the fact that the O-envelope trioxolane is at least as stable as its CC half-chair conformer. The stereochemical consequences of this mechanistic scheme, a symmetry allowed 1,3 dipolar cycloreversion, are abundantly discussed in ref 6b and will not be developed here. In brief, it rationalizes most of the stereochemical data, with a model more physically appealing than the phenomenological revisions of the Bauld-Bailey mechanism.

Acknowledgment. This problem originated from a most stimulating private communication from Professor R. W. Murray. The author is extremely grateful to Professor L. Salem for pointing out the surface crossing phenomena and for his constant encouragement.

References and Notes

(1) The Laboratoire de Chimie Théorique is associated with the C.N.R.S. (ERA No. 549).
(2) R. Criegee, *Rec. Chem. Prog.*, **18**, 111 (1957).
(3) (a) G. Schröder, *Chem. Ber.*, **95**, 733 (1962); (b) F. L. Greenwood and B. J. Haske, *Tetrahedron Lett.*, 631 (1965); (c) R. W. Murray, R. D. Youssefyeh, and R. P. Story, *J. Am. Chem. Soc.*, **89**, 2429 (1967), and references therein.
(4) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **88**, 3144 (1966).
(5) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Am. Chem. Soc.*, **90**, 1822 (1968).
(6) (a) R. P. Lattimer, C. W. Gillies, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **95**, 1348 (1973); (b) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *ibid.*, **96**, 348 (1974).
(7) C. W. Gillies and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **94**, 6377 (1972).
(8) Fliszár and Carles[9] suggested that this result can be consistent with a zwitterion path. However, their proposal has been contested by Murray and Higley.[10]
(9) S. Fliszár and J. Carles, *Can. J. Chem.*, **47**, 3921 (1969).
(10) R. W. Murray and D. P. Higléy, *J. Am. Chem. Soc.*, **95**, 7886 (1973), and references therein.
(11) C. Cupas, V. E. Watts, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2503 (1964).
(12) H. C. Brown, *Chem. Commun.*, 226 (1965).
(13) R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1103 (1971).
(14) P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Am. Chem. Soc.*, **93**, 3042 (1971), and references therein.
(15) R. P. Lattimer and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **96**, 6205 (1974).
(16) C. W. Gillies and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **94**, 7609 (1972).
(17) S. Fliszár and J. Carles, *J. Am. Chem. Soc.*, **91**, 2637 (1969).
(18) C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **96**, 1536 (1974).
(19) J. Castongway, M. Bertrand, J. Carles, S. Fliszár, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969).
(20) J. Renard and S. Fliszár, *J. Am. Chem. Soc.*, **92**, 2628 (1970).
(21) R. A. Rouse, *J. Am. Chem. Soc.*, **95**, 3460 (1973).
(22) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967).
(23) H. Staudinger, *Chem. Ber.*, **58**, 1088 (1925).
(24) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
(25) (a) P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burgess, *J. Am. Chem. Soc.*, **93**, 3044 (1971); (b) P. R. Story, E. A. Whited, and J. A. Alford, *ibid.*, **94**, 2143 (1972).
(26) P. S. Bailey, T. P. Carter, Jr., C. M. Fischer, and J. A. Thompson, *Can. J. Chem.*, **51**, 1278 (1973).
(27) B. J. Finlayson, J. N. Pitts, Jr., and H. Akimoto, *Chem. Phys. Lett.*, **12**, 495 (1972).
(28) R. Atkinson, B. J. Finlayson, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **95**, 7592 (1973).
(29) B. J. Finlayson, J. N. Pitts, Jr., and R. Atkinson, *J. Am. Chem. Soc.*, **96**, 5356 (1974), and references therein.
(30) H. E. O'Neal and C. Blumstein, *Int. J. Chem. Kinet.*, **5**, 397 (1973).
(31) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange No. 236, Indiana University, Bloomington, Ind.
(32) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1970); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).
(33) (a) T. H. Dumming, Jr., and W. A. Goddard III, *J. Chem. Phys.*, **62**, 3912 (1975); (b) W. A. Goddard III, T. H. Dumming, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).
(34) D. Grimbert and A. Devaquet, *Mol. Phys.*, **27**, 831 (1974).
(35) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).
(36) P. C. Hiberty, *J. Am. Chem. Soc.*, **97**, 5975 (1975).
(37) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).
(38) R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).
(39) The "puckering angle" is the dihedral angle between the C_1–O_1–O_2 plane and the C_1–C_2–O_3–O_2 plane.
(40) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).
(41) J. N. Pitts, Jr., private communication.
(42) In fact this stabilization seems to be slightly less important in extended basis set than in minimal one. As an example, the 3 × 3 CI stabilizes ozone by 63.7 kcal/mol in STO-3G basis and by 41.1 in 4-31G, which corresponds to a 2:3 ratio. Similarly, for the envelopelike transition state, the stabilization brought by the 3 × 3 CI with respect to the ground configuration is 24 kcal/mol in STO-3G and 38 in 4-31G. If we now draw curve II by subtracting from the ground configuration 4-31G energies of each point only two-thirds of the stabilization brought by the large CI in STO-3G, we find an activation energy of 17.1 kcal/mol, still in the limits of a room-temperature process.