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An AM1 Study of the Reactions of Ozone with Ethylene and 2-Butene

Michael J. S. Dewar,* Jackson C. Hwang, and Daniel R. Kuhn

Contribution from the Chemistry Department, The University of Texas at Austin, Austin, Texas 78712. *Received December 13, 1989. Revised Manuscript Received August 21, 1990*

Abstract: Detailed AM1 calculations are reported for the reactions of ozone with ethylene and with *cis*- and *trans*-2-butene. The results support the Criegee mechanisms and are consistent with the available experimental evidence. Implications concerning the stereochemistry of ozonolysis are discussed.

Introduction

Ozonolysis, the cleavage of olefins by ozone in solution, has been of continuing interest to chemists for over 100 years. Indeed it remains a standard tool in synthesis. The corresponding gas-phase reactions have also attracted attention recently because of their implication in the formation of photochemical smog.[1] Much attention has therefore been paid to the mechanisms of such reactions.

The Criegee Mechanism[2] (see Figure 1) is now generally thought to be the major process in most reactions of ozone with olefins in solution.[3] This involves three distinct steps. In the first, ozone adds directly to the olefin to form a cyclic adduct (**1**). This then dissociates to a mixture of a carbonyl compound and a carbonyl oxide (CO, **2**) which then recombine to form the ozonide (**3**). To avoid confusion, we will refer to **1** as the *primary oxonide* (PO) and to **3** as the *final ozonide* (FO). The CO is also commonly termed the *Criegee intermediate.*

It seems likely that this mechanism also predominates in the gas phase[4] rather than the alternative suggested by O'Neal and Blumstein.[5] While no CO (**2**) has been observed in the gas phase, a dioxirane, the product of the ring closure of the CO, has been detected by MW spectroscopy[6] as has the methyl-substituted FO (**3**).[7] Side reactions naturally predominate because of the lack of a solvent to carry off the heat generated in the reactions.

The forms of the transition states (TS) leading to **2** from the primary ozonide (**1**) and for the recombination of **2** with the corresponding carbonyl compound have been the subject of considerable debate, and a number of theoretical studies have been reported.

The results of two[8,9] of these can be discounted because of specific deficiencies in the methods used, i.e., MINDO/3[10] and MNDO.[11] MINDO/3 is known[10] to give energies that are much too negative for molecules containing pairs of adjacent heteroatoms, let alone *three* adjacent heteroatoms. It is therefore not surprising that it gave a heat of formation for the PO from ozone and olefin which was clearly far too negative. Equally, MNDO has encountered problems[12] in the case of cycloaddition reactions

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[4] (a) Dodge, M. C.; Arnts, R. R. *Int. J. Chem. Kinet.* **1979**, *11*, 399. (b) Herron, J. T.; Huie, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 5430.

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because the corresponding transition states (TS) usually contain very long bonds, falling in the region where MNDO overestimates interatomic repulsions.[11] The activation energy calculated for the first step (I) in eq 1 was therefore much too large (30 kcal/mol).

Several ab initio calculations have been reported.[13-20] These, however, also suffer from deficiencies of various kinds.

Goddard et al.[13] proposed, on the basis of GVB calculations, that processes I-III occur via biradical intermediates. They did not, however, locate or characterize the corresponding TSs. Since the GVB method also predicted[21] formation of an analogous biradical as the first step in the addition of singlet ($^1\Delta_g$) dioxygen to ethylene and since this prediction has been decisively refuted by experiment,[22] not much confidence can be placed in the corresponding prediction concerning ozone.

One of the other ab initio studies[16,17] compared Goddard's biradical pathway for step I (Figure 1) with the concerted pathway, both being found equally probable. The proposed energy profile, combined with ab initio reaction energies and experimental activation energies, seemed to provide a convincing picture of the overall reaction. However, the calculations were carried out by using very limited (3 × 3) CI. Since changes in correlation energy occur during ozonolysis, more effective allowance for electron correlation seems likely to be needed here.

No definite mechanistic conclusions can be drawn from any of the ab initio calculations that have been reported[15-18] because the TSs were either not calculated or not properly characterized.

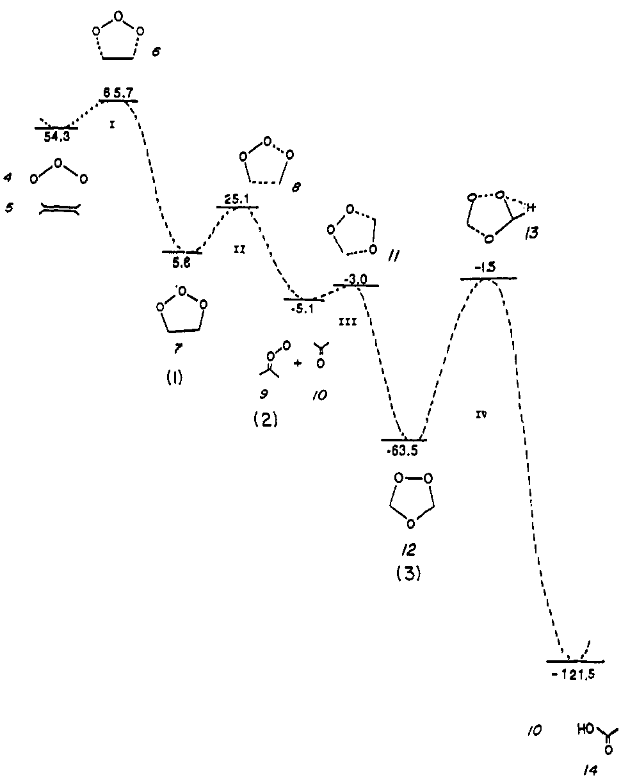
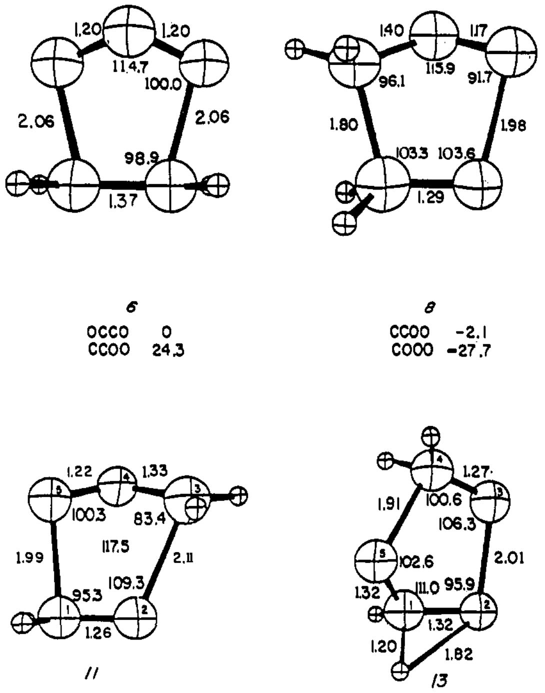


Figure 1. The reaction profile calculated by AM1 for ozonolysis of ethylene.



6
OCCO 0
CCOO 24.3

8
CCOO -2.1
COOO -27.7

11
5 1 2 3 10.8
1 2 3 4 18.5

13
1 2 3 4 23.4
2 3 4 5 2.6
3 4 5 1 -29.1

Figure 2. Geometries calculated by AM1 for transition states involved in the ozonolysis of ethylene: **6**, formation of the primary ozonide; **8**, dissociation of the primary ozonide into formaldehyde and CO; **11**, formation of the final ozonide; and **13**, decomposition of the final ozonide.

Although the PO, dioxirane, formaldehyde, and the FO have been observed as products of the ozone-ethylene reaction in a low-temperature microwave cell,[23] the available experimental evidence also fails to provide any definite conclusions concerning the mechanism of ozonization. The fact that only very small amounts of radicals could be detected in reactions carried out either in the gas phase[4] or in solution[24] suggests that biradical intermediates are not involved in any of the reactions (I-III) of eq 1. The same result would, however, hold if the lifetimes of the biradical intermediates were too short for them to take part in side reactions leading to single radicals. If biradicals are not involved, it is certainly difficult to see any viable alternative to the Criegee mechanism. Direct evidence for the latter has moreover been provided by studies[25] of secondary kinetic isotope effects which indicate that changes in bonding have taken place at *both* the relevant carbon atoms in the TSs of both II and III. The formation[4,24] of small amounts of radicals could be due to hot molecule processes, the addition of ozone to an olefin being highly exothermic.

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[17] Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3627.

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[20] Reference 3a, page 260.

[21] Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1980**, *102*, 439.

[22] Grdina, M. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111. While the authors are curiously diffident concerning the implications of their results, there is no question that they are in fact inconsistent with the mechanism proposed by Harding and Goddard. The observed kinetic isotope effects indicate that in the product-determining step of the reaction between singlet O_2 and $Me_2C{=}CMe_2$ methyl groups attached to the same carbon atom are nonequivalent, whereas methyl groups adjacent (syn) to one another on different carbon atoms are equivalent. This is clearly inconsistent with the intervention of a biradical ($^{\bullet}O{-}OCMe_2CMe_2^{\bullet}$) of the kind postulated by Harding and Goddard since here the oxygen atom abstracts hydrogen from one or the other of the methyl groups attached to the other radical center.

[23] (a) Zozom, J.; Gillies, C. W.; Suenram, R. D.; Lovas, F. *Chem. Phy. Lett.* **1987**, *139*, 64. (b) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. *J. Am. Chem. Soc.* **1988**, *110*, 7991.

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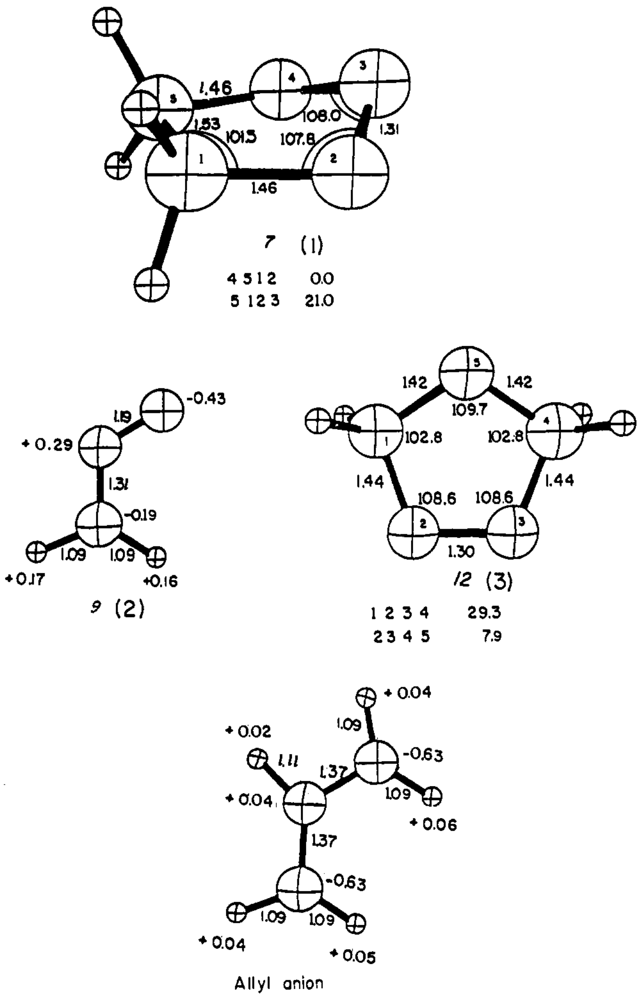

Figure 3. Geometries calculated by AM1 for allyl anion and species **7**(1), **9**(2), and **12**(3) involved in the ozonolysis of ethylene.

As indicated above, effective theoretical studies of ozonolysis have been hampered in the past by the need to use very high level ab initio procedures and by the inability of semiempirical ones to reproduce the heat of formation of ozone. Since these problems are avoided in the AM1 semiempirical SCF MO procedure,[26] and since this has proved very effective in applications to other pericyclic reactions,[27] we have now used it to study the reactions of ozone with ethylene and with *cis*- and *trans*-2-butene.

Procedure

All calculations were carried out by using the standard[26] version of AM1 as implemented in the AMPAC[28] package of computer programs. All geometries were optimized with respect to all geometrical parameters, without making any assumptions. TSs were located by the reaction coordinate method,[29] optimized by minimizing the scalar gradient of the energy,[30] and characterized by calculating force constants.[30]

Results and Discussion

A. Ozonolysis of Ethylene. Calculations were first carried out for the reaction of ozone (**4**) with ethylene (**5**). This was found to follow the Criegee mechanism (eq 1) as indicated by the reaction profile in Figure 1. The geometries calculated for the TSs are shown in Figure 2 and those for the PO (**7**), CO (**9**), and FO (**12**) in Figure 3. The individual reactions will henceforth be referred to by the corresponding Roman numerals (I–IV) in Figure 1. Table I shows the heats of formation calculated for the various species studied.

Table I. AM1 Heats of Formation of Stable Species

compd	heat of formation (kcal/mol) calcd	obsd
4	37.8^a	34.2^a
5	16.5^a	12.5^a
7	5.6	
9	26.4	
10	-31.5	
12	-63.5	
14	-97.4^a	-90.5^a
27	-3.2	
28	-4.7	
29	19.0	
30	20.3	
31	-71.7	
32	-72.6	
33	0.2	
propene	6.6^a	4.8^a
cis-2-butene	-2.2^a	-1.7^a
trans-2-butene	-3.3^a	-1.8^a
acetaldehyde	-41.6^a	-39.7^a

^{a}Reference 26.

Table II. Relative Energies (kcal/mol) of Stable Species Involved in Wittig Reactions, Calculated by Various Procedures

	ab initio HF^a				
compd	"D"	MPC	GCB	AM1	AM1 (corr)^b
4 + 5	(0)	(0)	(0)	(0)	(0)
7	-77.6	-49.2	-52.6	-48.7	-41
9 + 10	-67.7	-35.5	-42.6	-59.4	-51
12	-131.8	-98.6	-96.6	-117.8	-110
10 + 14	-208.1	-160.4		-175.8	-168^c

^{a}For description of basis sets and references, see text. ^{b}Allowing for the error in the heat of formation calculated for (**4** + **5**). ^{c}Observed, −163.1 kcal/mol.

The only species for which experimental heats of formation are available are the reactants (ozone (**4**) and ethylene (**5**)) and the final products of ozonolysis (formaldehyde (**10**) and formic acid (**14**)). The errors in the AM1 values for them are[26] +3.6, +4.0, −5.6, and −6.9 kcal/mol, respectively. These are all within the expected range for AM1, the average unsigned error for a varied collection of CHON compounds being 5.9 kcal/mol.[26] The error in the calculated heat of reaction for the overall conversion of (**4** + **5**) to (**10** + **14**) is, however, unusually large (20.1 kcal/mol), because the errors in the reactants and products all happen to act in the same direction, an unfortunate coincidence. If the reaction took place in a single step, or if our calculations referred only to a single example of ozonolysis, an error of this magnitude would be disturbing. Since the reaction in fact involves four different steps, the errors in the individual heats of reaction are likely to be much smaller. Furthermore, two-thirds of the error is due to errors in the energies calculated for the products (**10** + **14**) which are relevant only to dissociation of the secondary ozonide (**12**, reaction IV). These errors should have no effect on the reactions leading to **12**, which are the ones of primary interest here.

Cremer[15–17] has reported extensive calculations, by using various ab initio procedures, for the stable species indicated in Figure 1. The basis sets used ranged from STO-3G to a very large one ("D") of double-ζ plus polarization type. Corrections for correlation were made by using second-order Møller-Plesset perturbation theory (MP2). Geometries were fully optimized in all cases, except for **7** and **12** where RHF geometries were used in the MP2 calculation.

The values in Table I cannot usefully be compared with those from ab initio calculations, for well-known reasons.[31] Ab initio

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(26) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. P.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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(28) *QCPE Publication 506*; Department of Chemistry, Indiana University, Bloomington, IN 47405. An improved version (AMPAC2.1) is now available.

(29) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1971**, *93*, 4290.

(30) (a) McIver, J. W.; Komornicki, J. *J. Am. Chem. Soc.* **1972**, *94*, 2625. (b) McIver, J. W.; Komornicki, J. *Chem. Phys. Lett.* **1971**, *10*, 303.

methods can be used only to predict relative energies. Table II shows the energies calculated by Cremer for the intermediates and products in Figure 1, relative to those for the reactants. The values listed are for RHF calculations using the "D" basis set and for MP2 calculations using the "C" (6-31G*) basis set (MPC). GVB values reported by Goddard et al.[13] and our AM1 values are included for comparison. Since the energies listed in Table II are relative to that of the reactants (**4** + **5**), the AM1 values are all subject to the error (+7.6 kcal/mol) in the latter. A better comparison with other procedures is therefore provided by the correspondingly corrected values in the last column of Table II, and the subsequent discussion is based on them.

Table II also compares the calculated heats of reaction for the overall conversion of (**4** + **5**) to (**10** + **14**). The error in the best HF value is very large, ca. 50 kcal/mol. The error is more or less eliminated at the MP2 level, implying that it corresponds to a large change in correlation energy during the reaction. It is now generally agreed that ozone is the culprit, a conclusion supported by a recently described procedure[31] for estimating the effective errors in ab initio estimates for the energies of individual molecules. The errors for ozone are very large for all the models considered (STO-3G, 3-21G, 6-31G*).

The fact that HF procedures give energies for ozone that seem to be too positive has been noted in other connections. Thus the heats of reaction calculated for the isomerization of ozone to dioxygen are far too large. It has been generally assumed that this discrepancy indicates ozone to be a biradical-like species. However, while a biradical-like species cannot be represented adequately by a single-configuration wave function in a HF-type ab initio treatment, this does not mean that any species that cannot be represented by a single-configuration wave function is necessarily biradical-like. AM1 calculations seem to show unambiguously that ozone is not in fact significantly biradical-like. In the case of biradical-like species, open shell versions (UHF or HE-CI[28]) of AM1 invariably lead to heats of formation that are much more negative than those from the usual RHF version. In the case of ozone, however, all three procedures give similar results; i.e., RHF, 37.8; UHF, 33.4; HE-CI, 38.5 kcal/mol. The differences are similar to those for normal closed shell molecules with no biradical character. The unusually large correlation energy of ozone must therefore be due to some other factor, one that is treated adequately by the AM1 formalism where allowance for correlation is made by a Pariser–Parr-type adjustment of the electron repulsion integrals.

AM1 correctly predicts the rate-determining step in the overall ozonolysis of ethylene to formaldehyde and acetic acid to be the first (I in Figure 1), i.e., formation of the PO (**1**). The corresponding overall activation energy (11 kcal/mol) agrees with experiment (~5 kcal/mol[32]) to within the limits expected for AM1. These comments refer of course to the gas phase. In solution, where the intermediates are trapped by dissipation of the heat of reaction, the slowest step will be the one with the highest activation energy, starting from the previous stable species. According to our calculations, this should be II, as indeed seems to be the case.[33]

The AM1 value for the heat of reaction for reaction I is −41 kcal/mol, in line with Benson's thermochemical estimate[33] (−45 kcal/mol), Hiberty's 4-31G ab initio study[14] (−41 kcal/mol), Cremer's MP2 calculation[16] (−49 kcal/mol), and the GVB calculations by Harding and Goddard (−53 kcal/mol).

The structure (Figure 2) calculated for the TS (**6**) for reaction I has C_s symmetry. That for the PO (**7**) has an oxygen envelope (C_s) structure (Figure 3), in agreement with a recent experimental study and ab initio calculations by Cremer.[15] The lengths (1.31 Å) predicted for the O–O bonds in **7** are less than Cremer's value (1.45 Å) by 0.14 Å. This is as expected because AM1 underestimates[26] the lengths of *all* O–O bonds, both single and double, by ca. 0.15 Å. The lengths calculated for the C–C bond are in reasonable agreement (AM1, 1.53; Cremer, 1.55 Å).

The errors in AM1 O–O bond lengths, while large from the point of view of structural chemistry, are of little mechanistic significance, given that AM1 predicts the heats of formation of peroxides correctly. Thus the errors in the AM1 heats of formation for hydrogen peroxide, dimethyl peroxide, and diethyl peroxide are, respectively, −2.8, +3.0, and +7.7 kcal/mol.[26] As noted above, AM1 also gives a good estimate of the heat of formation of ozone even though the calculated bond lengths are too small by 0.12 Å. The rate of a reaction depends on the energies and entropies of the reactants and the TS, not on their geometries. An error in a calculated bond length is important only if it leads to an incorrect assessment of steric strain. The errors in O–O bond lengths cannot have significant effects of this kind in the present connection. They may lead at most to energies that are somewhat too positive for the cyclic species, i.e., primary and secondary ozonides, due to overestimation of ring strain in rings containing O–O bonds.

The geometry (Figure 2) calculated for the TS (**8**) for reaction II corresponds to a distorted envelope, as predicted by simple MO theory.[34] In the reverse reaction, **9** and **10** should approach one another in essentially parallel planes in order to maximize orbital overlap. Our calculated activation energy (20 kcal/mol) is larger than the experimental values (7 and 14 kcal/mol) for various alkyl-substituted POs.[35] The difference could, however, well be due to substituent effects since alkyl groups should make the reaction more exothermic, the carbon atoms adjacent to alkyl changing their hybridization from sp^3 to sp^2. This should lead to a corresponding decrease in the activation energy.

Reaction III was found to have a low heat of activation (2 kcal/mol), taking palce via the unsymmetrical TS **11** (Figure 2). While no quantitative experimental estimates have been reported, the calculated value is consistent with the available experimental evidence, and it also agrees with the GVB value (4 kcal/mol) calculated by Harding and Goddard. The bond that is formed more completely in the TS corresponds to attack by the terminal oxygen of **2** on the formaldehyde carbon, as would be expected intuitively. The geometry of the TS corresponds again to a distorted envelope, this leading to maximum orbital overlap. The structure calculated for the FO (**12**) had C_2 symmetry, as observed[36] and predicted by Cremer.[15] Our geometry agrees quite well with Cremer's except for the expected shortening of the O–O bonds (1.30 vs 1.47 Å).

Reaction IV, i.e., cleavage of **12** to **10** and **14**, may occur either in two steps via a biradical or in one step, migration of hydrogen accompanying ring cleavage. AM1 predicts the latter to be more favorable. As can be seen from Figure 2, hydrogen has migrated to a considerable extent in the TS (**13**), the C–H bond length having increased to 1.20 Å and the O–H distance having shortened to 1.83 Å. The lengths of the O–O (2.01 Å) and C–O (1.91 Å) bonds indicate that the former has, as usual, cleaved to a greater extent.

Similar comments apply to the FO (**12**). While no reliable experimental value seems to be available for the heat of formation of any ozonide, the corrected AM1 value (−110 kcal/mol) for the heat of reaction for the overall formation of **12** from (**4** + **5**) is in acceptable agreement with Cremer's estimate (−99 kcal/mol).

Problems arise, however, in the case of reaction II. AM1 predicts this to be quite strongly exothermic (ΔH, −11 kcal/mol), in agreement with Hiberty's estimate[14] (ΔH, −8 kcal/mol). However, Cremer's ab initio calculations (both D and MPC, Table II) predict it to be *endothermic* by a comparable amount (ΔH, +14 kcal/mol). The discrepancy (25 kcal/mol) is far outside the normal range of error for AM1.[26] Since the AM1 and ab initio errors for **10** seem to be small,[31] the difference must relate to the

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(33) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105.

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(35) Mile, B.; Morris, G. W.; Alcock, W. G. *J. Chem. Soc., Perkin Trans. II* **1979**, 1644.

CO (**9**). It cannot be attributed to the CO (**9**) being biradical-like because a UHF AM1 (UAM1) calculation led to an energy only a few kcal/mol lower than the AM1 value and because allowance for correlation led to little change in the ab initio heat of reaction for II.[16,17]

If Cremer's estimate were correct, the activation energy for the reverse of II, i.e., recombination of formaldehyde and CO to form PO, would have to be close to zero, because the estimated endothermicity (14 kcal/mol) of the forward reaction would be at least equal to the activation energies (7 and 14 kcal/mol[35]) observed for derivatives of **1**. This seems very unlikely. The fact that carbonyl oxide intermediates in ozonizations can be efficiently trapped[3] shows that there must[33] be a barrier to the alternative mode of recombination of **9** and **10** to form **12**, a process which is unquestionably far more exothermic ($-\Delta H > 40$ kcal/mol) than the alternative cycloaddition to form **7**. AM1 indeed predicts an activation barrier (2 kcal/mol) to the formation of **12**. Since AM1 has given good estimates of activation energies for a number of other cycloadditions of various types,[12,27] this prediction is likely to be correct. Similar comments apply to reaction II which AM1 predicts to be quite strongly exothermic and where the AM1 barrier agrees reasonably well with experiment. If the reaction is in fact endothermic, the AM1 barrier would be expected to be much too small.

These arguments seem to suggest rather strongly that the error lies in the ab initio value for the energy of **9** and that the AM1 results for reaction II are closer to the truth. Since no thermochemical data are available for carbonyl oxides or related species, the errors in the energies calculated for them by AM1 or by ab initio methods cannot be assessed. As noted above, ab initio estimates of relative energies can be trusted only when tests have indicated that the errors in the energies of the individual molecules should cancel. There are, moreover, specific reasons for believing that the AM1 value for **9** is nearer to the truth. AM1 has been applied, usually with success, to a wide range of "nonclassical" molecules. In the cases where it fails, e.g., in comparisons of classical and π complex forms of carbonium ions, the AM1 energies for the nonclassical species are too *positive*. It therefore seems extremely unlikely that the AM1 energy for **9** can be too *negative* by any large amount. Note also that, according to simple MO theory, **9** and ozone have analogous dipolar structures and that while AM1 gives a good estimate of the energy of **9**, RHF ab initio procedures give values that are much too positive.

The formal charges and geometry calculated by AM1 for **9** are shown in Figure 3. The charges in **9** alternate in a manner analogous to those in the isoelectronic allyl anion, which are also shown in Figure 3.

B. Ozonolysis of 2-Butene. As yet we have not considered another aspect of ozonolysis, namely the stereochemistry of the reaction in cases where ozone reacts with substituted olefins. Experiment indicates that in the case of bulky substituents, *cis*-olefins lead predominantly to cis FOs while *trans*-olefins lead mostly to trans FOs.[3] When the substituents are small alkyl groups, however, both *cis*- and *trans*-alkenes are found to give a cis-trans ratio of less than unity.[2,3]

Extensions of the Criegee mechanism, designed to rationalize these trends, have been based on the preferential formation of syn or anti substituted COs, the CO being the carrier of stereochemical information between the PO and FO. Early attempts along these lines were based on qualitative arguments concerning the preferred conformations of the PO and FO.[37] These qualitative treatments were based on two assumptions: (1) that the PO and FO are nonplanar and (2) that the principle of least motion[38] applies. If the first condition holds, a substituent (R) can occupy a pseudoaxial or a pseudoequatorial position in the ozonide, and the rates of the corresponding reactions should differ. The principle of least motion may then be used to predict which conformation, R axial or R equatorial, leads to syn or anti CO from the PO, and a similar argument can be applied to the subsequent conversion of the CO to the FO.

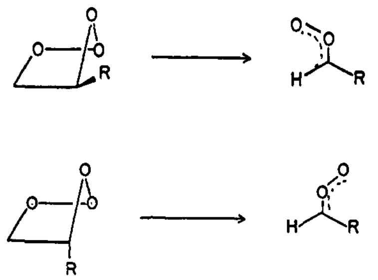

Figure 4. Processes leading to *syn*- and *anti*-acetaldehyde oxides.

Figure 4 shows the relationship between axial and equatorial substitution of the PO and the formation of syn or anti CO. While these approaches have yielded some useful qualitative relationships, difficulties arise in relating the conformations of the PO and FO to that of the corresponding TS. According to the Curtin–Hammett principle[39] the stability of the ground-state conformation has no influence on the course of a reaction unless the barrier to the reaction is lower than that of interconversion of the conformers. This seems unlikely to be the case here. Indeed, HF/SCF calculations predict facile conformational interconversion for both the PO[40] and the FO.[41] Arguments based on the conformation of the PO or FO are moreover valid only if the TS for reaction II is a very early one of if that for reaction III is a very late one, neither of which is the case. While reaction II may be exothermic, there is no reason to believe that the TS is "early" enough to be truly reactant-like. The same objection applies even more forcefully to reaction III, the reaction having an "early" TS which would not be expected to be influenced by the structure of the product. Cremer's study indicated that the PO from a small alkene cleaves via a TS which favors the formation of syn CO rather than anti CO, while POs with bulky substituents decompose via early TSs, due to an increase in the exothermicity of step II.[17] While Cremer has tried to predict properties of the TSs from his studies[16,17,40,41] of the PO and FO conformations, he did not carry out calculations for them.

Any attempt to explain these results by theoretical calculations encounters two major objections. First, the differences in stereochemistry correspond to very small differences in energy, far smaller than the possible errors in molecular energies calculated by *any* current procedure. And secondly, the experimental results refer to reactions in solution, whereas the calculations refer to the gas phase. Indeed, in many cases the product ratios are solvent dependent.

Concerning the first objection, any procedure is likely to give better estimates of differences in energy between closely related systems than of absolute energies. Thus numerous examples are known where theoretical calculations reproduce small differences between closely related isomers or between similar reactions. Calculations can therefore serve as a check on assumed mechanisms and suggest alternatives, even if they are not accurate enough in an absolute sense to lead to a priori predictions. Calculations can also provide information concerning the structures of transition states which is not available from experiment.

Concerning the second objection, this situation holds in practically all current theoretical studies of reactions. However, knowledge of the way a given reaction takes place in the gas phase can often provide information concerning its mechanism in solution, and comparison of the courses taken by a reaction in the gas phase and in solution can also indicate how the solvent operates.

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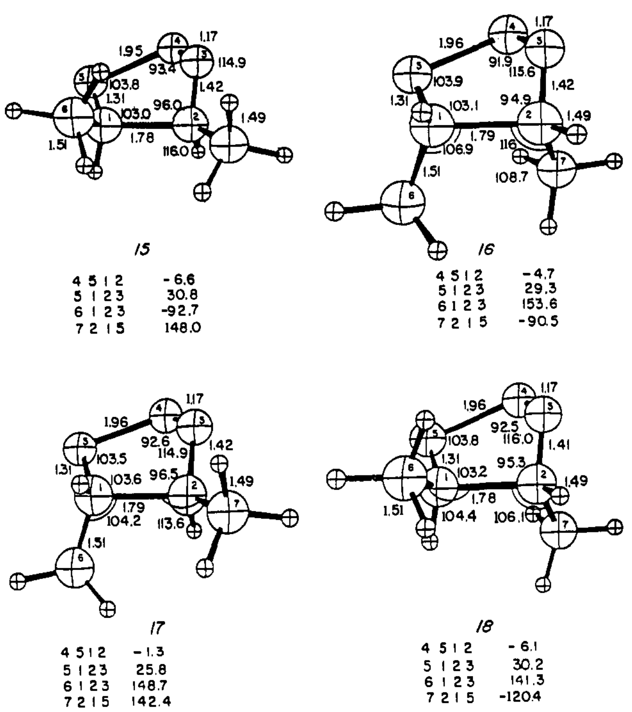
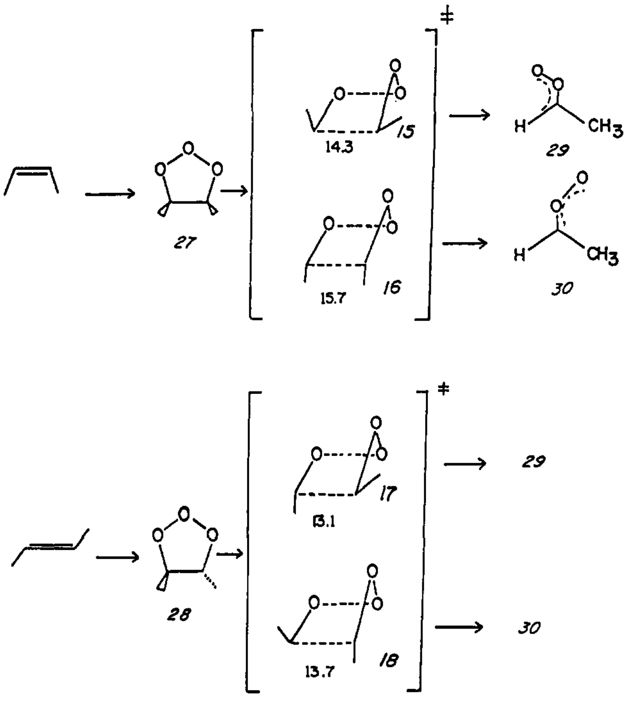


Figure 5. AM1 geometries of TSs involved in the decomposition of the primary ozonides from 2-butene.

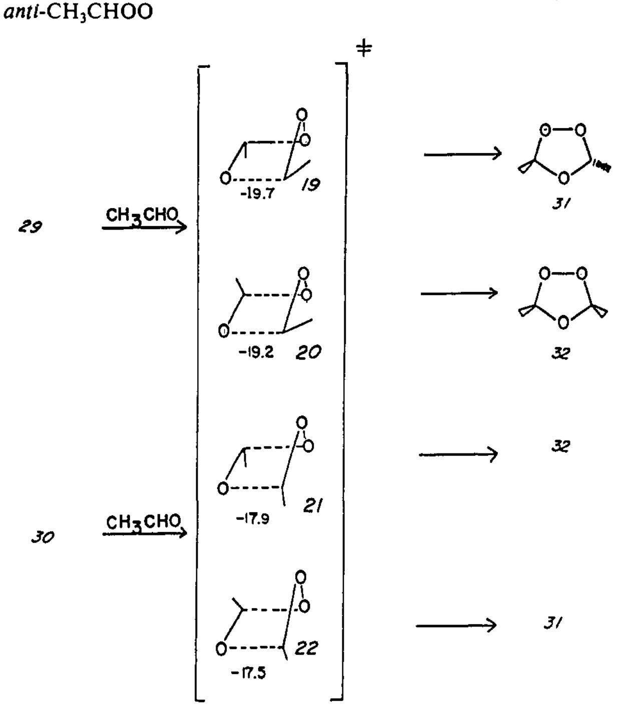
Scheme I. Processes Leading from *cis*- and *trans*-2-Butene and O_3 to *syn*- and *anti*-CH_3CHOO and Acetaldehyde



We therefore decided to study the ozonolyses of *cis*- and *trans*-2-butene in detail, by using AM1.

Scheme I shows the processes leading from *cis*- and *trans*-2-butene to the *anti*-**29** and *syn*-**30** COs, along with the energies calculated by AM1 for the TSs. The corresponding geometries are shown in Figure 5. The TSs are little deformed from the envelope structure predicted for the parent, as would be expected in view of the relatively small size of the alkyl groups. For decomposition of the cis PO,[27] AM1 predicts a lower activation energy for reaction via **15** (14.3 kcal/mol) than via **16** (15.7 kcal/mol), implying preferential formation of the less stable anti CO **29**. AM1 predicts the syn CO **30** to be the more stable by 1.3 kcal/mol, in agreement with calculations by other procedures.[3a]

Scheme II. Formation of *cis*- and *trans*-2-Butene FO from *syn*- and *anti*-CH_3CHOO



The anti CO **29** is also predicted to be the major product from decomposition of the trans PO **28**, the energy of the corresponding TS **17** being lower by 0.6 kcal/mol. Cremer has suggested that the tendency for methyl to be equatorial in the envelope conformation of the PO[34] and in the corresponding TS[16,17] is due to the enhanced interaction between it and the two occupied antibonding MOs of the trioxirane ring.

The activation energies for reaction III between acetaldehyde and **29** or **30** have been predicted to be quite low (<5 kcal/mol), due to favorable dipole interactions between the aldehyde and the CO.[16] If this is the case, the TSs should be reactant-like and their energies should run parallel to those of the COs. Thus in Scheme II, the TSs **21** and **22** resulting from the reaction of the more stable syn CO **30** should be favored. We do indeed predict very low activation barriers for these reactions, ranging from 1.6 to 5.1 kcal/mol. However, as can be seen from Scheme II, the TSs (**19** and **20**) for reactions of the anti CO **29** are predicted to be the more stable. While this can be attributed[16,40] to stabilization of **19** and **20** (Figure 6) by the "π effect", dipole interactions may also play a role, as Cremer has suggested. Scheme II indicates that the trans FO **31** should be the main product from the anti CO **29**. Since both *cis*- and *trans*-butene PO lead preferentially to formation of the anti carbonyl oxide, *trans*-butene FO should be the major product in both cases as indeed it is.[3]

Cross ozonolysis of propene with added acetaldehyde results mainly in *cis*-butene FO. Since Scheme II applies to the formation of butene FO by a cross ozonide reaction, from propene PO and added acetaldehyde, preferential formation of the syn CO **30** in the decomposition of propene PO **33** would conform to the experimental findings. However, AM1 predicts **33**, like the *cis*-butene **27** and *trans*-butene **28** POs, to give preferentially the anti CO **29**. Scheme III shows our results for the decomposition of **33** while Figure 7 shows the geometries calculated for the TSs. From the arguments above, there seems to be no good reason why the factors favoring the equatorial-substituted TS should not be as valid with propene PO as with the butene POs. The difference may, however, be due to solvent effects. The cis/trans ratios are indeed known[25b] to vary with solvent. The two reactions may moreover be affected differently because reaction of the CO with added aldehyde must occur outside the original solvent cage, while this need not be so for the recombination of the CO and aldehyde formed by cleavage of 2-butene PO. Indeed, since the calculated activation energies for the formation of butene FO are so small

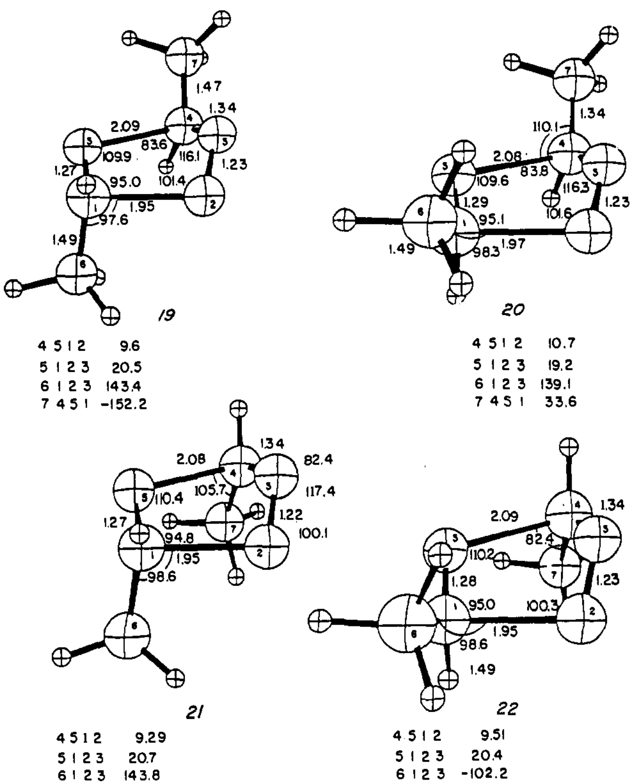
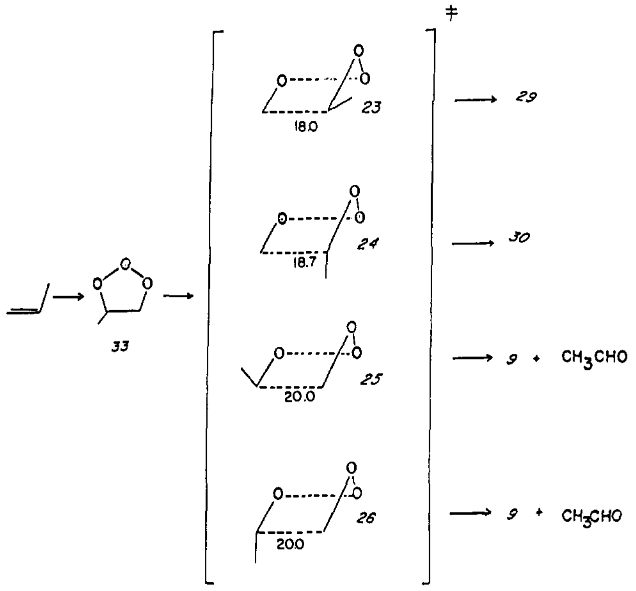


Figure 6. AM1 geometries of TSs for the formation of 2-butene final ozonides from acetaldehyde oxide and acetaldehyde.

Scheme III. Processes Leading from Propene and O_3 to CH_3CHOO, CH_2OO, CH_3CHO, and CH_2O



(1.6–5.1 kcal/mol), it seems likely that virtually all of its results from recombination inside the solvent cage.

These results could also be explained if **29** and **30** equilibriate before stage III of the reaction. Since **30** is predicted to be more stable than **29** by ca. 1 kcal/mol, this would lead to the correct stereochemistry. There is, however, no direct evidence that the COs can undergo geometrical isomerization, and theoretical calculations have predicted the corresponding barriers to be large.[42]

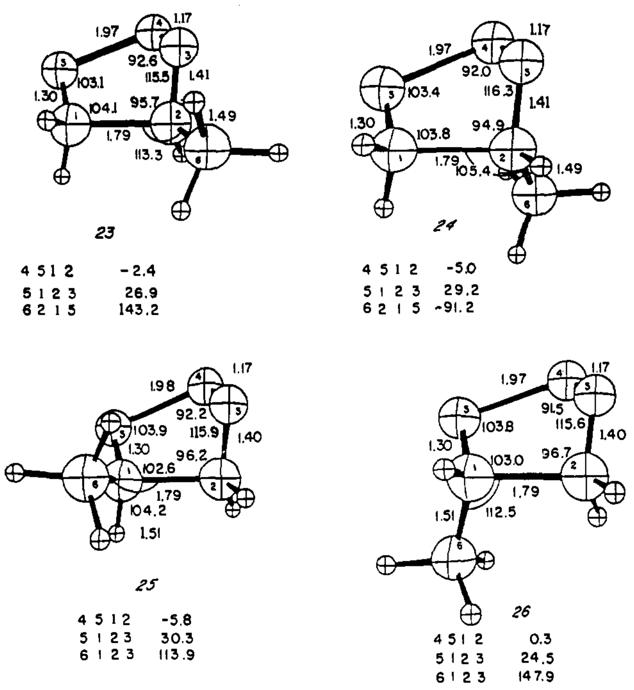


Figure 7. AM1 geometries for TSs for the decomposition of propene primary ozonide.

We have found that AM1 also predicts a high barrier (27.0 kcal/mol) for inversion of **9** by in-plane flipping of oxygen. In the case of rotation about the C=O bond, the easiest path for inversion is by reversible isomerization to dioxirane (**34**). The calculated barrier for this process is also large (34.4 kcal/mol), and **34** is moreover predicted to be lower in energy than **9** by 8.4 kcal/mol, in agreement with current evidence that dioxiranes are lower in energy than isomeric carbonyl oxides.

A second possibility is that the reaction in solution is of desolvation barrier (DSB) type,[43] the activation barrier corresponding to desolvation of the reactants. The rather large dipole moments calculated for **30** (4.1 D) and **29** (4.5 D) make this seem reasonable. If the formation of the FO in solution is indeed a DSB process, the calculations reported here (see Scheme II) would have no direct relevance to it since they refer to the gas phase. The same would be true for other current explanations of the stereochemistry of butene cross ozonides. The stereochemistry of the butene ozonides formed by ozonolysis of propene may then be controlled by factors entirely different from those operating in the case of *cis*- and *trans*-2-butene.

The formation of the butene cross ozonide depends, of course, on the formation of **29** or **30** in the decomposition of propene PO. Propene PO **33** can also decompose to **9** and acetaldehyde (see Scheme III). The ratio of (**29** + **30**) to **9** has been determined[44] by trapping experiments, leading to an ca. 1.6:1 preference for the former. The AM1 results are consistent with this conclusion, the TSs leading to **29** or **30** being more stable by 1–3 kcal/mol than those leading to **9**.

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Registry No. **5**, 74-85-1; **7**, 6669-36-9; **9**, 78894-19-6; **12**, 289-14-5; **27**, 15981-73-4; **28**, 15981-77-8; **29**, 65339-04-0; **30**, 65339-03-9; **31**, 16187-15-8; **32**, 16187-01-2; **33**, 35476-71-2; **34**, 157-26-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; propene, 115-07-1; acetaldehyde, 75-07-0; allyl anion, 1724-46-5.

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