

Theoretical Determination of Molecular Structure and Conformation. 18. On the Formation of Epoxides during the Ozonolysis of Alkenes

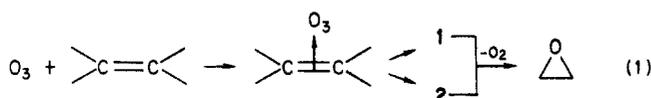
Dieter Cremer* and Charles W. Bock

Contribution from the Lehrstuhl für Theoretische Chemie, Universität Köln, 5 Köln 41, West Germany, and Philadelphia College of Textiles & Science, Department of Chemistry, Philadelphia, Pennsylvania 19144. Received August 30, 1985

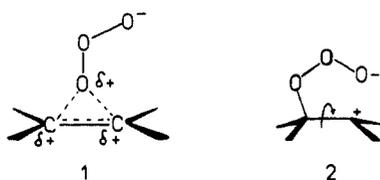
Abstract: The reaction of carbonyl oxide (CH_2OO) and ethylene has been investigated by ab initio techniques. According to theoretical results, carbonyl oxide can act as an oxygen-transfer agent, thus leading to epoxide and aldehyde: $\text{C}_2\text{H}_4 + \text{CH}_2\text{OO} \rightarrow \text{CH}_2\text{OCH}_2 + \text{CH}_2\text{O}$. The calculated transition-state energies of the various epoxidation modes are 4–8 kcal/mol, which are comparable to activation energies of cycloaddition (cycloreversion) reactions encountered in the ozonolysis of alkenes. Epoxidation of alkene by carbonyl oxide is best described as a $\text{S}_{\text{N}}2$ reaction on the terminal oxygen atom of carbonyl oxide. The preferred collision mode of the O-transfer reaction can be rationalized on the basis of frontier orbital interactions. Apart from epoxidation, carbonyl oxide can add to ethylene, yielding 1,2-dioxolane. The energy requirements of the cycloaddition are equivalent to those of the epoxidation. However, 1,2-dioxolanes will only be observed under normal ozonolysis conditions if the excess energy generated in the cycloaddition reaction is readily dissipated. Otherwise, 1,2-dioxolanes will immediately decompose, again yielding, among other products, epoxides.

Epoxides are known to be "partial cleavage" products of the ozonolysis of alkenes, olefins with various other functional groups, and related compounds such as allenes and ketenes.¹ Epoxide formation does not conform with the Criegee mechanism of ozonolysis, which proceeds via 1,2,3-trioxolane (primary ozonide, PO) formation, decomposition of PO to carbonyl oxide and aldehyde, and subsequent recombination of the decomposition products to 1,2,4-trioxolane (final ozonide, FO).¹⁻⁴ In principle, ozone, PO, and carbonyl oxide can act as oxygen-transfer agents since all three coexist under normal ozonolysis conditions.

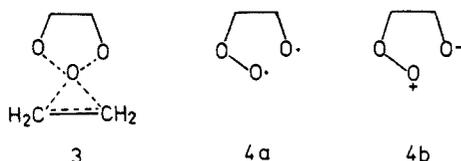
There are many cases where ozone is likely to be the epoxidation agent.¹ Ozone can form a π -complex with (electron-rich) alkenes which then may decompose via transition state (TS) 1 or zwitterion 2 to epoxide and oxygen (reaction 1) rather than leading to PO.⁵



Reaction 1 is probably valid in those cases where molecular oxygen is observed as a product in comparable molar quantities with the epoxide. For sterically hindered alkenes epoxidation is stereospecific, suggesting that 1 is an intermediate. For alkenes with substituents that stabilize the positive carbon atom in 2, a non stereospecific (stereoselective) reaction can be expected.^{1,5}



Apart from ozone, PO may be considered as a potential epoxidation agent. The oxygen transfer could occur via TS 3 or by cleavage of PO to the diradical (zwitterion) 4a (4b) which then



acts as the actual O transmitter. A TS such as 3 has recently been discussed for the degenerate oxygen-transfer reaction between oxirane and ethylene on the basis of ab initio calculations.⁶ However, the activation energy of such a reaction seems to be far too high (~ 35 kcal/mol⁶) to be accessible during the ozonation of alkenes. Also, the decomposition of PO to 4a or 4b is energetically unfavorable compared to PO cleavage to carbonyl oxide and aldehyde.⁷

Finally, epoxide formation can be the result of a reaction between carbonyl oxide, the PO cleavage product, and unreacted alkene.⁸⁻¹³ Since equal amounts of carbonyl oxide and alkene are required for the reaction, the epoxide yield will be less than 50% in this case. Also, molecular oxygen will not be obtained in equal amounts with epoxide.

Murray and co-workers¹² have shown that carbonyl oxide, produced via singlet oxygen oxidation of diazo compounds, can epoxidize alkenes. Their results confirm an earlier suggestion by Kwart and Hoffman¹⁴ that carbonyl oxide obtained under non-ozonolysis conditions will act as an epoxidizing agent. Also, decomposition of ozone-free samples of the trioxolane of *trans*-di-*tert*-butylethylene has provided evidence that epoxidation can be caused by carbonyl oxide.¹³

Various modes of attack of carbonyl oxide at an alkene double bond are shown in Figure 1, 5a-5f. 5a-5d are analogous to TS

- (1) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, 1978 and 1982; Vol. I, Chapter X and XI, Vol. II, Chapter XII.
- (2) Criegee, R. *Angew. Chem.* **1975**, *87*, 765-771.
- (3) Kuczkowsky, R. L. "1,3-Dipolar Cycloaddition of Ozone and Carbonyl Oxides". In *1,3-Dipolar Cycloadditions*; Padwa, A. W., Ed.; Wiley: New York, 1984.
- (4) (a) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3619-3626. (b) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3627-3633. (c) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3633-3638.
- (5) Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473-4479.
- (6) Bach, R. D.; Wolber, G. *J. Am. Chem. Soc.* **1984**, *106*, 1410-1415.
- (7) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105-3115.
- (8) (a) Hamilton, G. A.; Giacini, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 1584-1585. (b) Keay, R. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 6876-6878; **1976**, *98*, 6578-6582.
- (9) Gillies, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 1276-1277; **1977**, *99*, 7239-7245.
- (10) (a) Griesbaum, K.; Brüggemann, J. *Adv. Chem. Ser.* **1972**, *112*, 50-64. (b) Griesbaum, K.; Brüggemann, J. *Chem. Ber.* **1972**, *105*, 3638-3649.
- (c) Griesbaum, K.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 2877-2881.
- (11) Moriarty, R. M.; White, K. B.; Chin, A. *J. Am. Chem. Soc.* **1978**, *100*, 5582-5584.
- (12) (a) Hinrichs, T. H.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 1282-1284. (b) Agarwal, S. K.; Murray, R. W. *Photochem. Photobiol.* **1982**, *35*, 31-35.
- (13) Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 7681-7682.
- (14) Kwart, H.; Hoffman, D. M. *J. Org. Chem.* **1966**, *31*, 419-425.

* Current address: Lehrstuhl für Theoretische Chemie, Universität Köln, 5 Köln 41, West Germany.

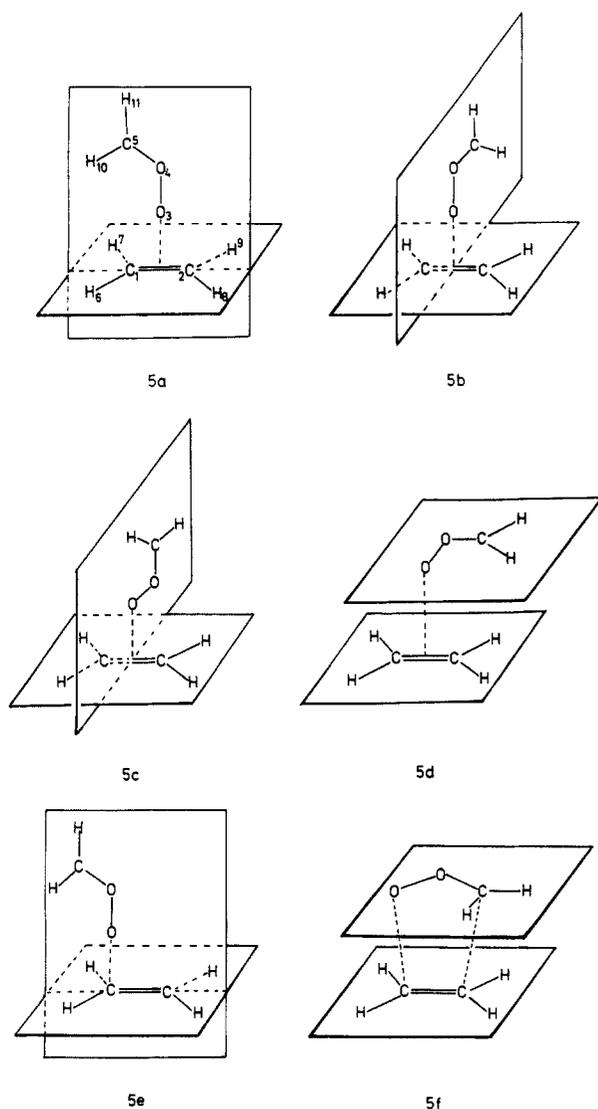
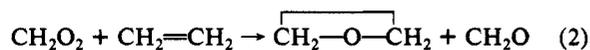
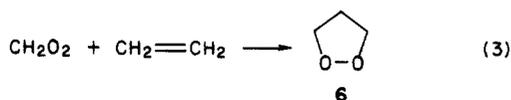


Figure 1. Different modes of attack of carbonyl oxide at the ethylene double bond. Reference planes and numbering of atoms (5a) are shown.

1 and should lead stereospecifically to epoxide and aldehyde (reaction 2). If, however, 5e is traversed, epoxidation will be



nonstereospecific for the same reason as discussed in the case of reaction 1. Alternatively, carbonyl oxide and alkene may react in a concerted fashion via 5f to yield 1,2-dioxolane (6) (reaction 3). 6, in turn, may decompose to epoxide.



In this work we will investigate the various reactions between carbonyl oxide and ethylene by ab initio techniques. Our work is part of a larger project^{4,15,16} aimed at an elucidation of the ozonolysis mechanism where particular emphasis is given to a description of carbonyl oxides,¹⁶ peroxy intermediates, which have not been described by experimental methods so far.

Numerical Methods

In an earlier investigation,¹⁶ it has been demonstrated that carbonyl oxides are satisfactorily described with augmented (DZ+P) basis sets estimating correlation corrections with the aid of second-order Møller-

Plesset (MP2) perturbation theory.¹⁷ Therefore, we have used Pople's 6-31G* basis¹⁸ in conjunction with MP2 theory in order to obtain reasonable energy differences of reactions involving carbonyl oxide. Due to calculational limitations we could not employ this level of theory for the search of TSs 5a-5f. Various attempts to explore the relevant reaction paths with smaller basis sets of DZ quality failed since either an unreasonable TS geometry or no TS at all was found. This has to do with the fact that the MP2/DZ (as well as the HF/DZ) OO bond length of carbonyl oxide is unreasonably long (e.g., MP2/4-31G: $R(\text{OO}) = 1.659 \text{ \AA}$, $R(\text{CO}) = 1.212 \text{ \AA}$ ¹⁶). Accordingly, OO bond rupture requires only a negligible amount of energy at these levels of theory.

In order to get at least a qualitative insight into the TS structures in question, we carried out Hartree-Fock (HF) STO-3G calculations,¹⁹ which provide better geometries and relative energies than either HF/DZ, HF/DZ+P, or MP2/DZ calculations. In previous investigations on peroxy compounds, it was shown that this is due to a fortuitous cancellation of basis set and correlation errors.¹⁵

Geometries of reactants and TSs have been determined by applying gradient techniques. In the case of the TSs, it has explicitly been checked whether the Hessian matrix of the function $E(\mathbf{R})$ possesses one and only one negative eigenvalue.²⁰ Geometrical parameters have been optimized within the following symmetry constraints. 5a, 5b, 5c, 5e: starting symmetry is C_2 , attack of the terminal O atom of carbonyl oxide is at the midpoint of the CC bond (5a-5c) or at C_1 (5e), hydrogens are allowed to move out of the planes shown in Figure 1, and a total of 18 parameters has been optimized. 5d: symmetry is C_1 , attack of the terminal O atom of carbonyl oxide is at the midpoint of the CC bond, the heavy atoms of carbonyl oxide and ethylene are in planes parallel to each other, hydrogens are allowed to move out of these planes, and a total of 23 parameters has been optimized. 5f: symmetry is C_1 , in the beginning of the cycloaddition reaction atoms of carbonyl oxide and ethylene are in planes parallel to each other, upon approach all atoms are allowed to move out of reference planes, and 25 parameters have been optimized.

Results and Discussions

In Table I energies of reactants and products of reactions 1, 2, and 3 are listed together with known or derived heats of formations and reaction enthalpies.²¹ Calculated TS energies and geometries are given in Table II; Mulliken charges are given in Table III.

Epoxidation by Carbonyl Oxide. Of the four "edge-directed" collision modes between carbonyl oxide and ethylene shown in Figure 1, only the first two lead to genuine TSs (5a and 5b) with one imaginary frequency. TSs 5a and 5b possess the same energy, 8.2 kcal/mol at the HF/STO-3G level and 4.7 kcal/mol at the HF/6-31G* level (Table II), with a marginal preference for 5a. This should, however, change as soon as either alkene or CO bear bulky substituents. In this case, 5b rather than 5a should be energetically more favorable since steric repulsion between the two reaction partners is minimized in this collision mode. Therefore, we will primarily consider TS 5b in the following discussion.

For collision modes 5c and 5d no TS was found. At an ethylene-carbonyl oxide distance equivalent to that of 5b (5a), the relative energies of 5c and 5d are 30-40 kcal/mol higher than those of TS 5b (5a) (Table II); that is, collision modes 5c and 5d are not energetically accessible under normal ozonolysis conditions.¹⁻⁴

The increase in energy when going from 5b to either 5c or 5d becomes readily apparent when considering interactions between the frontier orbitals of ethylene and carbonyl oxide (Figure 2). In 5b, the HOMO of carbonyl oxide ($\pi_2(a'')$) can overlap with the LUMO of ethylene ($\pi^*(a'')$) to yield the asymmetrical Walsh MO of oxirane and the π -MO of formaldehyde (interaction 1, Figure 2a). This interaction is enhanced by electron-acceptor

(17) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618-622. (b) Pople, J. A.; Binkley, S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1-19.

(18) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

(19) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657-2664.

(20) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625-2633.

(21) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970. For the ΔH_f° value of carbonyl oxide, see ref 4b.

(15) Cremer, D. *J. Chem. Phys.* **1978**, *69*, 4440-4455, 4456-4471; **1979**, *70*, 1898-1910, 1911-1927, 1928-1938.

(16) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199-7205.

Table I. Calculated Energies and Experimental Heats of Formation^a

molecule	HF/STO-3G ^b	HF/6-31G* ^b	MP2/6-31G* ^b	MP2/6-31G* ^c	$\Delta H^\circ_{f,298}$ ^d
O ₂ ^e	-149.634 17	-149.613 21	-149.953 33	-149.954 30	0
O ₃	<i>f</i>	<i>f</i>	-224.876 70	-224.876 83	34.8
H ₂ C=CH ₂	-77.073 95	-78.030 37	-78.293 62	-78.294 31	12.5
CH ₂ OO	-186.057 39	-188.552 19	-189.043 94	-189.052 83	38
H ₂ COCH ₂	-150.928 50	-152.864 52	-153.315 13	-153.315 56	-12.6
CH ₂ O	-122.354 35	-113.863 70	-114.173 75	-114.174 94	-25.9
(6)	-263.370 75	-266.697 26	-267.468 21		-13.8 ^g
reaction 1	<i>f</i>	<i>f</i>	-39.0	-39.4	-37.4
reaction 2	-95.1	-91.4	-95.0	-90.0	-89.0
reaction 3	-150.2	-72.0	-82.0		-64.3

^a Absolute energies in hartree, reaction energies and enthalpies in kcal/mol. The following HF/STO-3G geometries have been used. O₂, C₂H₄, CH₂O: Lathan, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *2*, 175-261. CH₂OCH₂: Lathan, W. A.; Radom, L.; Hariharan, P. C.; Hehre, W. J.; Pople, J. A. *Top. Curr. Chem.* **1973**, *40*, 1-45. O₃: $R(\text{OO}) = 1.287 \text{ \AA}$, $\angle \text{OOO} = 116.3^\circ$. CH₂OO: $R(\text{CO}) = 1.256 \text{ \AA}$, $R(\text{OO}) = 1.429 \text{ \AA}$, $R(\text{CH}_2) = 1.094 \text{ \AA}$, $R(\text{CH}_1) = 1.094 \text{ \AA}$, $\angle \text{OOC} = 120.0^\circ$, $\angle \text{OCH}_2 = 121.2^\circ$, $\angle \text{OCH}_1 = 118.9^\circ$. MP2/6-31G* geometries: O₂: $R(\text{OO}) = 1.247 \text{ \AA}$. O₃: $R(\text{OO}) = 1.301 \text{ \AA}$, $\angle \text{OOO} = 117.4^\circ$. C₂H₄: $R(\text{CC}) = 1.336 \text{ \AA}$, $R(\text{CH}) = 1.084 \text{ \AA}$, $\angle \text{CCH} = 121.7^\circ$. CH₂OO: ref 15. CH₂OCH₂: ref 30. CH₂O: $R(\text{CO}) = 1.220 \text{ \AA}$, $R(\text{CH}) = 1.104 \text{ \AA}$, $\angle \text{OCH} = 122.2^\circ$. For 6 the geometry specified in ref 35 has been used. ^b HF/STO-3G geometry. ^c MP2/6-31G* geometry. ^d From refs 4b and 21. ^e Energy (enthalpy) of the $^3\Sigma_g^-$ ground state. The $^1\Delta_g$ excited state formed in reaction 1 is 22.5 kcal/mol above $^3\Sigma_g^-$. ^f Energy (enthalpy) of reaction 1 has been obtained by considering the $^3\Sigma_g^- - ^1\Delta_g$ energy difference. ^g HF yields the wrong ground state for O₃. ^h Determined by using the calculated energy difference between 1,3-dioxolane and 1,2-dioxolane.³⁵

Table II. Calculated Energies and Geometries of 5a-5f^a

parameter	5a	5b	5c	5d	5e	5f
HF/STO-3G	-263.118 27	-263.118 19	-263.071 37	-263.062 41	-263.109 75	-263.122 21
	8.2	8.3	37.6	43.3	13.5	5.7
HF/6-31G*	-266.574 94	-266.575 14				-266.564 94
	4.8	4.7				11.1
TS ^b	yes	yes	no	no	yes	yes
$R((1,2)3)^c$	2.048	2.046	2.05 ^d	2.05 ^d	1.874	2.342
$R(1,2)$	1.320	1.320	1.310	1.314	1.326	1.327
$R(3,4)$	1.752	1.756	1.437	1.367	1.898	1.371
$R(4,5)$	1.225	1.224	1.251	1.271	1.221	1.279
$R(1,6)^e$	1.082	1.082	1.081	1.080	1.082	1.081
$R(5,10)^e$	1.100	1.100	1.095	1.089	1.101	1.090
$\angle(1,2)3,4^e$	179.7	179.5	90 ^d	90 ^d	153.9	114.9 ^f
$\angle 3,4,5$	116.9	116.8	119.5	120.0	117.3	116.1
$\angle 1,2,6^e$	122.0	122.0	122.2	122.2	121.5	121.8
$\angle 4,5,10$	122.2	122.2	121.2	121.2	122.5	120.8
$\angle 4,5,11$	121.6	121.6	119.1	117.7	122.1	117.6
$\tau(\text{CCH})^g$	1.6-2.1	1.6-2.0	12.1-13.1	8.6-13.4	1.2-9.6	3.5-11.1
$\tau(\text{OCH})^g$	0	0	0	0	0	21.9, 173.4

^a Absolute energies in hartree, relative energies in kcal/mol, distances in Å, and angles in deg. ^b A transition state (TS) is encountered if the Hessian matrix possesses one and only one negative eigenvalue. ^c (1,2) is the midpoint of the CC bond. In the case of 5e the angle $\angle 1,3,4$ is given. ^d Assumed values, see text. ^e Only averaged values are given. The actual parameters differ by less than 0.003 Å and 1°, respectively. ^f Angle between COO, CCH, and OCH, respectively, and corresponding reference plane shown in Figure 1.

Table III. Mulliken Charges Calculated for Transition States 5a and 5b^a

atom	5a			5b		
	total	π	σ	total	π	σ
C5	5.843	0.613		5.842	0.617	
O4	8.367	1.359	1.649	8.367	1.359	1.651
O3	8.262	1.986	0.346	8.263	1.936	0.346
C1	6.322		0.948	6.314		
C2	6.307		0.925	6.314		

^a HF/6-31G* values. " σ -charges" correspond to calculated P_y populations where the y -direction is roughly parallel to the OO axis. Compare with Figure 1.

substituents like CN groups in TCNE which lower the energy of the ethylene LUMO. As for the HOMO of ethylene ($\pi(a')$), this can overlap with a low-lying $\sigma^*(a')$ -MO of carbonyl oxide (interaction 2, Figure 2). Since the latter is OO antibonding, a charge transfer from ethylene weakens the OO bond and accelerates O transfer. This is also evidenced by the fact that interaction 2 yields the symmetrical all-bonding Walsh MO of oxirane and the σ -(CO)-MO of formaldehyde. Thus interactions 1 and 2 lower the energy of TS 5b and facilitate OC bond formation and OO bond rupture. Similar considerations apply to TS 5a, only that the

highest lone-pair (n) MO rather than the highest π -MO of carbonyl oxide has to be considered.

In the case of 5d, frontier orbital interactions comprise a four-electron destabilizing one, namely, the interaction between the π -MO of ethylene and the π_2 -MO of carbonyl oxide, which is shown in Figure 2b. Accordingly, the relative energy of 5d is significantly higher than that of 5b. CO bond formation and OO bond rupture will no longer be supported by frontier orbital interactions if carbonyl oxide and ethylene approach each other in parallel planes. The same holds for 5c. There, the four-electron-destabilizing interaction results from overlap between the π -MO of the alkene and one of the n orbitals at the terminal O atom of carbonyl oxide.

On first sight, one may designate epoxidation reaction 2 via TS 5b as a simple S_N2 displacement on oxygen leading to oxirane and formaldehyde in their ground states (GS). More careful considerations, however, reveal that excited states of H₂CO may also be formed. To prove this point we describe the electron configuration of 5 by just considering the occupation of oxygen 2p orbitals and ignoring low-lying and doubly occupied s orbitals.²²

(22) Cremer, D. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 1.

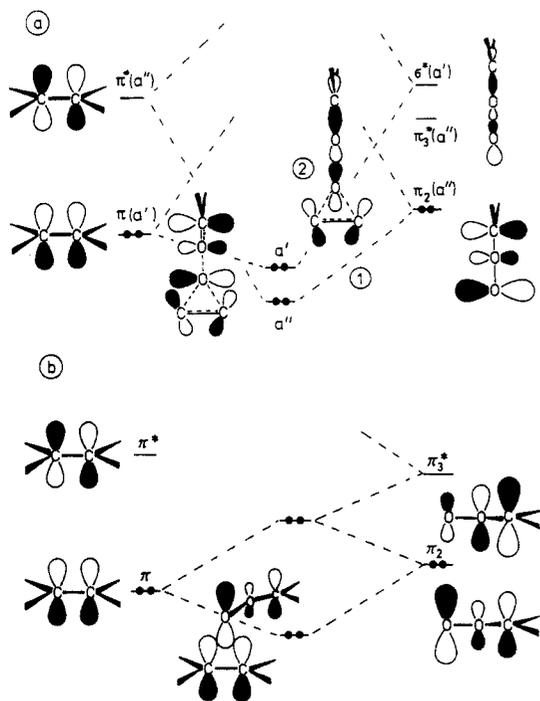


Figure 2. Frontier orbital interactions in the case of TSs **5b** (a) and **5d** (b), respectively.

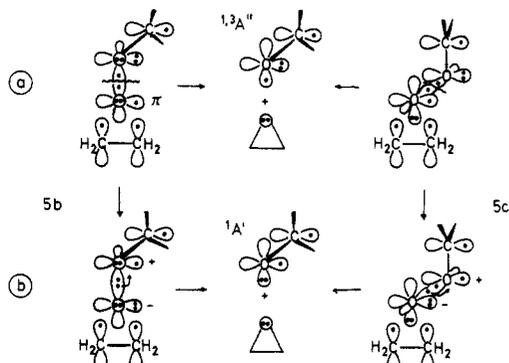


Figure 3. Schematic representation of the electron configuration of **5b** and **5c**. Only p (sp) orbitals are shown. Electrons are denoted by dots. (a) Homolytic OO cleavage; (b) heterolytic OO cleavage accompanied by charge transfer from O3 to O4.

In this way, the schematic representations of the electron configuration of **5b** and **5c** given in Figure 3a are obtained. They clearly reveal the biradical character of carbonyl oxide.^{16,23} As a consequence of this biradical character, OO bond rupture should lead to H₂CO either in its ³A'' or ¹A' excited state.

Alternatively, a polarization of the π -cloud toward the terminal O atom of carbonyl oxide may occur in TSs **5**, thus lending the carbonyl oxide entity some zwitterionic character as indicated in Figure 3b. It is very well-known that appropriate electron-releasing substituents at the carbon atom and/or polar solvents lead to a zwitterionic GS of carbonyl oxide.²³ If the polarized electron configuration shown in Figure 3b applies to TS **5b** (**5c**), then aldehyde will be formed in its GS. In this case, reaction 2 can be described as a S_N2 reaction on O with a heterolytic cleavage of the OO bond.

The electron distribution calculated for TS **5b** is in line with the latter possibility.²⁴ While the central oxygen atom bears the

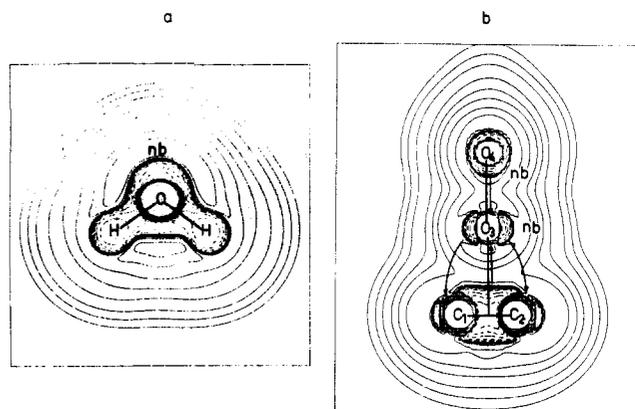


Figure 4. Contour line diagrams of the calculated (HF/6-31G*) Laplace concentrations, $-\nabla^2\rho(r)$, of H₂O (a) and TS **5b** (b). Molecular regions with charge concentration are indicated by dashed contour lines, those with charge depletion by (weak) solid contour lines. Heavy solid lines denote paths of maximum electron density linking atomic nuclei. The reference plane in (b) contains the C atoms of ethylene and the OO atoms of carbonyl oxide (compare with Figure 1). Arrows indicate directions of nucleophilic attack.

highest gross atomic charge (Table III), the highest p π -population, however, is found for the terminal oxygen atom. This is true for both TSs **5a** and **5b**.

One might ask how a nucleophilic attack on an electron-rich atom like oxygen is possible. An electrophilic attack should be much more likely. We have investigated this question by calculating the Laplace field $\nabla^2\rho(r)$ of the one-electron density distribution $\rho(r)$ for collision modes **5a** and **5b**. The Laplacian of $\rho(r)$ indicates in which regions of a molecule the electron density is concentrated ($\nabla^2\rho(r) < 0$) or depleted ($\nabla^2\rho(r) > 0$).^{25,26} On the basis of simple models, concentration lumps can be assigned to bonding and nonbonding electrons.²⁶ In the case of a divalent oxygen atom, two bonding and two nonbonding concentrations surround the nucleus, shielding it in all directions against a nucleophilic attack (Figure 4a). This is no longer true in the case of the terminal O atom of carbonyl oxide in TS **5b** (**5a**). Figure 4 shows a contour line diagram of the Laplace concentration of TS **5b** calculated for the plane containing the C atoms of ethylene and the O atoms of carbonyl oxide. In the direction of the OO axis, there are two concentration holes in the valence sphere of the terminal O atom of carbonyl oxide. A quantitative analysis of $\nabla^2\rho(r)$ reveals that the bonding concentration of ethylene as well as the nonbonding concentration at O4 of carbonyl oxide (Figure 4b) is polarized toward these concentration holes. The nonbonding concentration at O4 can be considered as the result of an heterolytic cleavage of the OO bond, withdrawing " σ -" concentration²⁷ from the terminal O atom and leading to the two concentration holes.

There are concentration lumps at the terminal O atom in the direction of the p π -orbital. These are indicative of the polarization of the π -density of carbonyl oxide upon reaction with ethylene.²⁸ In the way that the distance to ethylene decreases, these " π -" lumps distort toward the concentration holes at the ethylene C atoms (indicated by arrows in Figure 4) and form the CO bonding concentrations of oxirane. This process can be thought of as the result of orbital interaction 1 depicted in Figure 2a.

Also shown in Figure 4 are the paths of maximum electron density²⁹ linking the various atoms. The terminal O atom of

(25) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *54*, 1259-1281 and references cited therein.

(26) (a) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594-1605. (b) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627-628.

(27) If the total one-electron density distribution $\rho(r)$ is considered, there will be, of course, no difference between " σ -" and " π -" density. The term " σ -" concentration is only used to draw a connection between Figures 3b and 4b.

(28) Alternatively, carbonyl oxide can already be in a zwitterionic state due to substituent or solvent effects.^{22,23}

(23) (a) Harding, L. B. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180-7188. (b) Hiberty, P. C. *Isr. J. Chem.* **1983**, *23*, 10-20. (c) See also ref 22, Table 8.

(24) A caveat, however, is appropriate since the single-determinant description used in this work may artificially favor a polarized or zwitterionic electron structure.

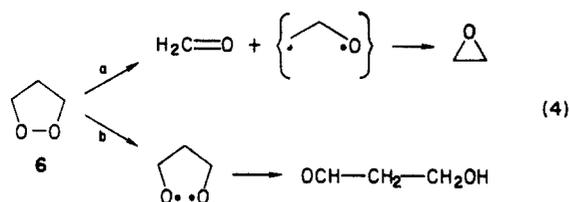
carbonyl oxide is connected by such a path to the midpoint of the CC bond of ethylene. This is typical for an alkene π -complex as was recently shown by Cremer and Kraka.³⁰ In summary, both electron density and concentration of TS **5b** (**5a**) are in line with a S_N2 reaction of O or an "oxene" transfer (Figure 4b) leading directly to oxirane and the GS of H_2CO .

Reaction 2 is about 50 kcal/mol more exothermic than epoxidation of ethylene by O_3 (reaction 1, Table I). The calculated reaction energy of -90 kcal/mol (MP2/6-31G*//MP2/6-31G*) is in accord with the reaction enthalpy based on a theoretical ΔH_f° value of carbonyl oxide given by Cremer.^{4b} The $^3A''$ and $^1A''$ excited states of H_2CO are 72.0 and 80.6 kcal/mol above the $^1A'$ GS of H_2CO ;³¹ that is, their formation via reaction 2 would still be exothermic, namely, by 18 and 10 kcal/mol. The formation of H_2CO ($^1A''$) in the gas-phase ozonolysis has been proven by chemiluminescence.³² Therefore, this work does not fully exclude homolytic OO cleavage (Figure 3) and formation of $^1,3A''$ form-aldehyde.³³

The O transfer via TS **5b** should be stereospecific. If, however, the alkene participating in reaction 2 possesses a strongly polarized double bond due to substituent effects, then the formation of epoxide may occur via **5e**. The calculated energy of TS **5e** is only 5 kcal/mol higher than that of TS **5b** (Table II). If **5e** is traversed, then rotation at the CC bond will be possible and the epoxidation will be no longer stereospecific.

Formation of 1,2-Dioxolanes. Apart from an O transfer via reaction 2, carbonyl oxide can react with ethylene in a concerted fashion according to reaction 3. The TS of the cycloaddition reaction is shown in Figure 1, **5f**; its energy and geometry are given in Table II. Calculated activation energies are 5.7 (HF/STO-3G) and 12.4 kcal/mol (HF/6-31G*). Even if one considers these results only of qualitative value, the fact that the energies of **5b** and **5f** are quite similar provides sufficient evidence for a possible competition of cycloaddition 3 and O-transfer reaction 2.

The best value for the theoretical reaction energy is close to -64 kcal/mol; that is, cycloaddition 3 is also very exothermic and **6** is formed as a hot molecule with an excess energy of 78-85 kcal/mol. On the other hand, the dissociation energy of the OO bond in **6** is less than 38 kcal/mol.^{34,35} This means that in the



gas phase, **6** will immediately decompose, whereas the cycloreversion path **a** probably requires less energy than a hydrogen transfer yielding a γ -hydroxy aldehyde.³⁶

In solution phase, however, energy dissipation will be possible, in particular if **6** bears one or more substituents. For example, in the ozonolysis POs are formed with an excess energy of about

(29) Any lateral displacement from the path of maximum electron density leads to a decrease in $\rho(r)$. It has been shown that the necessary condition for a covalent bond between two atoms is a path of maximum electron density linking the corresponding nuclei.²⁵

(30) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800-3810, 3811-3819.

(31) Herzberg, G. *Molecular Spectra and Molecular Structure, III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand: New York, 1966.

(32) Atkinson, R.; Finlayson, B. J.; Pitts, J. N. *J. Am. Chem. Soc.* **1973**, *95*, 7592-7599 and references cited therein.

(33) Murray, R. W.; Ramachandran, V. *J. Org. Chem.* **1983**, *48*, 813-816. These authors have observed chemiluminescence in the condensed phase upon heating poly(carbonyl oxide).

(34) The dissociation energy of the OO bond of **6** can be estimated from that of MeOOME (38 kcal/mol) and the strain of the five-membered ring (~5 kcal/mol) to be about 33 kcal/mol. See ref 22, Chapter IV.C.

(35) Cremer, D. *Isr. J. Chem.* **1983**, *23*, 72-84.

(36) Hydrogen or alkyl migration at the stage of the 1,3-diradical can lead to another aldehyde (ketone).

50 kcal/mol.^{4b} Nevertheless, they possess a lifetime in solution phase sufficient for detection by NMR spectroscopy.^{1,7} In this connection it is interesting to note that Keul and Kuczkowski have recently synthesized the first 1,2-dioxolane via ozonolysis of methyl vinyl ether.³⁷ These authors assume a competition between unreacted enol ether and methyl formate for cycloaddition with carbonyl oxide where both methyl formate and carbonyl oxide are the cleavage products of the corresponding PO. Since the enol ether possesses a greater dipolarophilicity than the ester, 1,2-dioxolane is formed.

Another experimental result relevant to a possible involvement of carbonyl oxides in the formation of 1,2-dioxolanes has been reported by Nojima and co-workers.³⁸ These authors discovered that 1,2-dioxolanes are formed when boron trifluoride-diethyl ether is added to a solution of an alkene and a FO. The reaction most likely proceeds via acid-mediated decomposition of FO to carbonyl oxide and aldehyde and subsequent addition of carbonyl oxide to alkene. The reaction conditions, however, are such that only BF_3 -coordinated carbonyl oxide will be formed in the decomposition step. Accordingly, the addition reaction should be non-concerted, as outlined by Nojima.³⁸

Conclusions

(1) Carbonyl oxides can epoxidize alkenes via TS **5a** or **5b**. The calculated activation energies are comparable to those encountered in the ozonolysis reaction.⁴ Since cycloaddition reactions of carbonyl oxide with either aldehydes or alkenes bearing bulky substituents are energetically demanding, reaction 2 (besides reaction 1) should become in this case the main source of epoxide formation.

(2) In solution phase the O transfer from carbonyl oxide to alkene is best described as a S_N2 reaction on oxygen. The analysis of $\rho(r)$ and $\nabla^2\rho(r)$ in TSs **5a** and **5b** suggests an heterolytic cleavage of the OO bond. However, a homolytic cleavage of this bond leading to either the $^1A''$ or $^3A''$ excited state of aldehyde cannot fully be excluded, in particular, if epoxidation takes place in the gas phase.

(3) 1,2-Dioxolane formation as recently observed by Keul and Kuczkowski³⁷ in the ozonolysis of methyl vinyl ether is a result of a cycloaddition of carbonyl oxide to unreacted alkene. The energy barrier of this reaction is comparable to that of the epoxidation reaction but will strongly depend on the nature of the alkene substituents. 1,2-Dioxolane is formed as a hot molecule and, therefore, will decompose in the gas phase immediately. In solution phase, energy dissipation becomes possible. Accordingly, 1,2-dioxolanes are expected to be more frequently byproducts of the ozonolysis than is generally assumed.

(4) While this work provides evidence that carbonyl oxides can act as O-transfer agents during the ozonolysis of alkenes, it cannot exclude that carbonyl oxide related compounds play also an important role in epoxidation reactions. For example, Murray and Ramachandran³³ have elegantly shown that cyclic poly(carbonyl oxides) epoxidize alkenes. Furthermore, dioxiranes may lead to epoxides. In both cases, however, the actual epoxidation agent may be carbonyl oxide, formed by oligomer decomposition or ring opening. Work is in progress to investigate these possibilities.

Acknowledgment. Support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Rechenzentrum der Universität Köln, and the Computer Center of the Philadelphia College of Textiles & Science is gratefully acknowledged. Discussions with Prof. R. W. Murray and Prof. K. Schank have stimulated this work. We thank an unknown referee for suggesting **5a**.

(37) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370.

(38) Yoshida, M.; Miura, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1983**, *105*, 6279-6284. See also: Miura, M.; Yoshida, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Chem. Commun.* **1982**, 397-398. This process probably involves two steps and is definitely less exothermic due to the fact that it is started from a peroxy-carbenium ion ($RRC^+-OOF_3^-$) rather than carbonyl oxide.