A Molecular Orbital Study of the Mechanism of the Oxidation of Acetylene by Peroxyformic Acid

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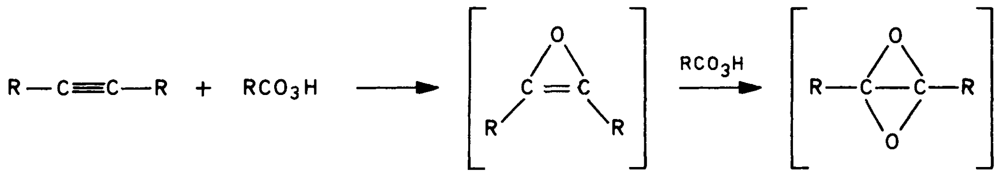
The restricted Hartree–Fock level of *ab initio* theory has been used to study the reaction of peroxyformic acid with acetylene. Various plausible directions of the peroxy-acid approach to acetylene, believed to lead to molecular arrangements of both components which are near the transition state for the formation of oxiren, were investigated. The unsymmetrical attack of the peroxy-acid on acetylene is energetically more favourable than the symmetrical one. The peroxy-acid approach appears to be dominated by charge-transfer interactions. Theoretical investigation of the second-step of reaction, *i.e.* the oxidation of oxiren to 2,4-dioxabicyclo[1.1.0]butane, shows that such a molecule cannot exist. Nevertheless, the possibility of a diradical state for this species cannot be ruled out.

ALTHOUGH mechanistic studies on the oxidation of acetylenes with peroxy-acids are not as abundant as those for olefins, enough data are now available for a theoretical treatment of this reaction.[1]

At least theoretically, monoepoxidation of acetylenes should first produce oxirens, which could be further converted into dioxabicyclo-derivatives, *e.g.* 2,4-dioxabicyclo[1.1.0]butanes, as shown in Scheme 1. Neither of these intermediates has yet been detected. However, oxidation of acetylenes with peroxy-acids usually gives a mixture of products which have been explained on the basis of these two intermediates. In particular, experimental evidence for the involvement of oxirens in these reactions is beginning to accumulate.[2] It was only recently that 1,2-hydrogen shift in both the peroxy-acid and enzymatic oxidation of a triple bond was unambiguously demonstrated by studying the fate of the deuterium on the oxidation of monodeuteriated biphenyl-2-ylacetylene. Nearly quantitative retention of deuteriation in the esterified biphenyl-2-ylacetic acid was found, thus indicating that this oxidation involves reaction of the reagent with the π-electrons (oxiren formation) rather than with the terminal C–H bond of acetylene (hydroxyacetylene formation) (Scheme 2).[3]

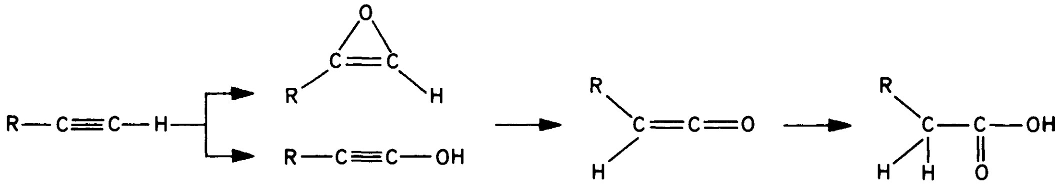


SCHEME 1

In general, acetylenes react considerably slower with peroxy-acids compared to structurally similar olefins.[4,5] Oxidation of oct-4-yne with *m*-chloroperoxybenzoic acid in various solvents capable of intermolecular association with peroxy-acids revealed that peroxy-acid–solvent interactions play a similar role in the oxidation of this compound as well as in epoxidation of cyclohexene. A linear free-energy relationship with a slope of 1 was obtained by correlating the logarithmic rates of oct-4-yne oxidation with those of epoxidation of cyclohexene with the trend of activation parameters also being the same.[5]

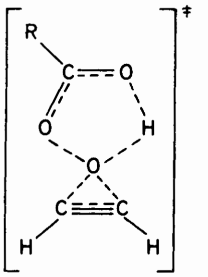
All the above mentioned evidence seem strongly to support oxiren as the first intermediate in these reactions. Oxirens are of theoretical interest as models of 4π-electron antiaromatic molecules.[6] These species could, in principle, exist in equilibrium with oxocarbenes. Therefore, it is quite possible that both kinds of intermediates are involved in the reaction.

In this paper, small regions of the potential energy hypersurface for the interaction of acetylene and oxiren with peroxyformic acid were examined by the restricted Hartree-Fock level of *ab initio* theory. Basically, two mechanistic hypotheses were tested. The first one is the 1,1-addition mechanism with a symmetrical (' butterfly ') transition state (*A*), first proposed by Bartlett,[7] or an unsymmetrical transition state (*B*), suggested by Waters.[8] The second mechanistic proposal involves a 1,3-dipolar addition of a more or less developed hydroxy-

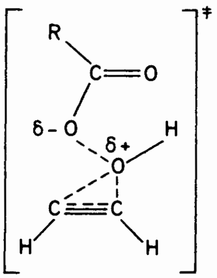


SCHEME 2

carbonyl oxide (derived from the intramolecularly hydrogen bonded peroxy-acid) to an unsaturated dipolarophile [transition state (*C*)].[9]



(*A*)



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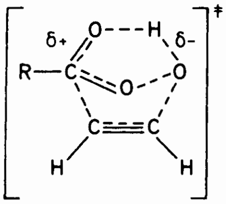


(*C*)

CALCULATIONS

The *ab initio* computations were performed in the LCAO-MO-SCF scheme using contractions of primitive Gaussian functions. Three basis sets were employed. Owing to the size of the molecules, the minimal STO-2G basis set was used to calculate molecular geometries.[10] As shown previously, this basis set gives nearly the same geometry parameters as the STO-3G basis set.[10] Molecular energies and Mulliken populations were then calculated by using the STO-4G basis set. For the final energy comparison the extended basis set (6-31G) was used.[11]

RESULTS AND DISCUSSION

Peroxyformic and Formic Acids.—The optimized geometries and all other data were taken from our previous study.[12]

HCO_3H. R(H–C) = 1.090 Å; R(C=O) = 1.225 Å; R(C–O) = 1.394 Å; R(O–O) = 1.402 Å; R(O–H) = 1.009 Å; H–$\hat{C}$=O = 127.2°; O–$\hat{C}$=O = 122.7°; C–$\hat{O}$–O = 110.3°; O–$\hat{O}$–H = 100.9°. It is worth mentioning that the calculated dipole moment (μ = 2.26 D; 6-31G) of the chelated form is in excellent agreement with that determined experimentally for higher aliphatic peroxy-acids (μ = 2.32 D).[13]

HCO_2H. R(H–C) = 1.009 Å; R(C=O) = 1.227 Å; R(C–O) = 1.375 Å; R(O–H) = 0.994 Å; H–$\hat{C}$=O = 120.3°; O=$\hat{C}$–O = 126.9°; C–$\hat{O}$–H = 104.5°.

Acetylene. R(H–C) = 1.075 Å (1.061 Å);[14] R(C≡C) = 1.178 Å (1.203 Å).

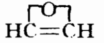
Oxiren. R(C=C) = 1.276 Å (1.261 Å);[6c] R(C–O) = 1.487 Å (1.548 Å); R(H–C) = 1.080 Å (1.057 Å); H–$\hat{C}$=C = 156.8° (162.5°).

The Approach of Peroxyformic Acid to Acetylene.—It is at present practically impossible to calculate a complete energy hypersurface for a system as large as HCO_3H + HC≡CH even within a Hartree–Fock approximation, especially in view of the rather great difficulties in obtaining a satisfactory potential for peroxides as well as the uncertainty concerning the nature of the initially formed intermediate. Therefore, we were forced to introduce some approximations. Initially, several arbitrarily chosen directions of the peroxy-acid approach to acetylene, selected on the basis of chemical intuition, were chosen for the investigation. The minimization procedure along these reaction co-ordinates was assumed to give molecular arrangements of both components that are near the transition state. The calculated ' plausible transition states ' most probably do not have zero derivatives for displacement along the assumed co-ordinates.[15] The procedure was to minimize all geometrical variables indicated in structures (1)—(5) [α in structures (1)—(4), and α and β (other than 90°), in (5), as well as the geometry of the acetylenic part of these structures] as a function of distance R. The exception was the basic geometry of the peroxy-acid part of the ' transition state ' which was taken from our previous study.[12a] This is believed to be not too great an approximation in view of rather great similarity of both reactions.

Equilibrium energies of ' transition states ' are, together with distances R, collected in Table 1. All attempts to locate a minimum equilibrium energy of structures (2)—(4) failed. Equilibrium geometries of most stable molecular arrangements are shown in Figure 2. The process(es) proceeding through the 'transition state' to products was (were) not investigated.

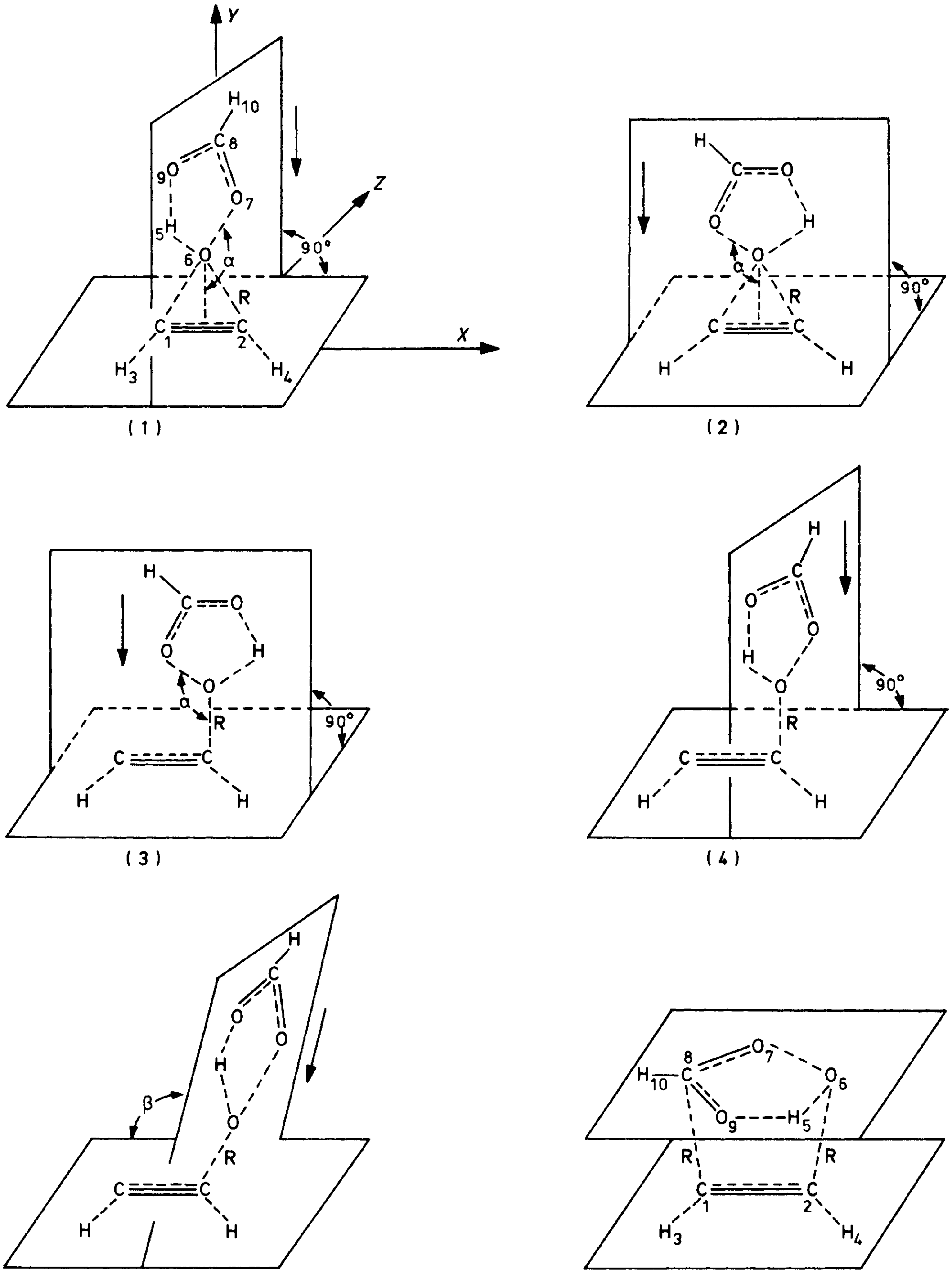
TABLE 1

Equilibrium energies of and distances (R) in the ' transition state '. Equilibrium energies of reactants and products

' Transition state '	R/Å	E (a.u.) STO-4G	E (a.u.) 6-31G
(1)	3.00	−338.256 52	
(5)	3.15	−338.256 99	−340.142 35
(6)	3.26: 3.48	−338.257 37	
HC≡CH		−76.407 25	−76.791 34
HCO_2H		−187.551 75	−188.658 44
:HCO_3H		−261.874 09	−263.369 85
 HC=CH		−150.704 09 (−150.699 61) [a]	−151.505 30 (−151.510 64) [a]

[a] The geometry was taken from ref. 6*c*.

From the mechanistic point of view, we compare the obtained results with our study of the oxidation of ethylene with peroxyformic acid.[12a] It is seen from Table 1 that the approach distance, R, is longer than is the corresponding one in the peroxy-acid–ethylene system (R = 2.35—2.86 Å). The Mulliken population analysis shows that in all molecular arrangements investigated electrons are transferred from acetylene to peroxyformic acid (Table 2) (electrophilic stage of the reaction) indicating a charge-transfer interaction between both components.[16] The most favourable approach of the peroxy-acid, as evident from structures (1) and (5) in Figure 2, is such as to allow maximum interaction be-



(1) (2) (3) (4) (5) (6)

FIGURE 1 Various directions (1)—(6) of peroxy-acid approach to acetylene

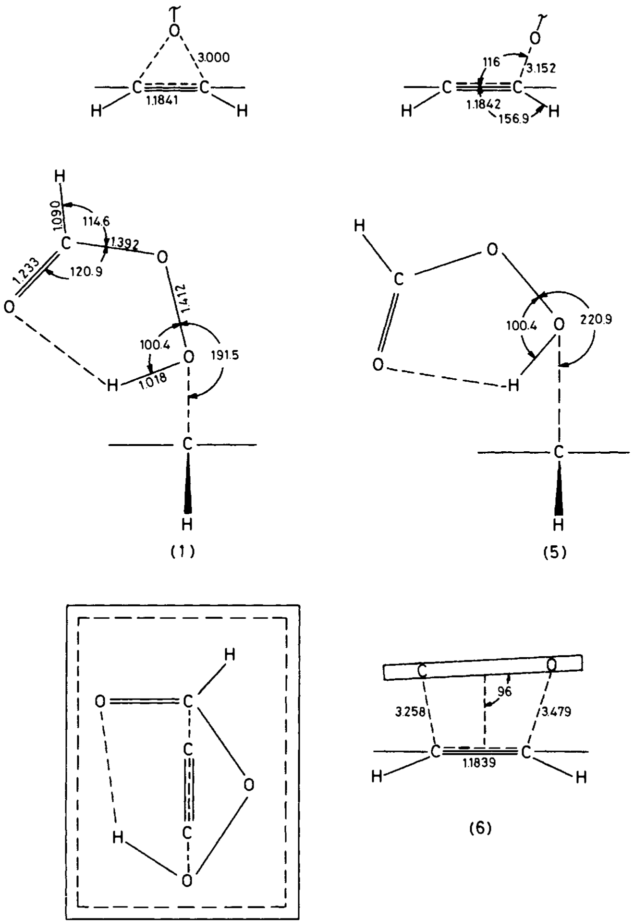


Figure 2 The equilibrium geometries of the ' transition states ' (1), (5), and (6). Bond lengths and angles are in Å and °, respectively

tween the electron deficient p_y orbital of the oxygen atom bond to hydrogen (the oxygen–oxygen axis) as well as the lowest unoccupied (LUMO) antibonding σ^* orbital oriented in the same direction of the peroxy-acid [12b] and the highest occupied (HOMO) π orbital of acetylene.

Assuming the 1,1-addition mechanism to be valid, it is evident that unsymmetrical attack of the peroxy-acid on acetylene is energetically more favourable than the symmetrical one (C_s symmetry). This finding seems to support the Waters' proposal, *i.e.* an unsymmetrical approach of the peroxy-acid in a direction having an H–$\hat{C}$–PA angle of 87°, which is considerably smaller than that predicted by Baldwin for the attack of electrophiles on the same substrate (H–$\hat{C}$–E *ca.* 120°).[17] We do not have any reasonable explanation for this discrepancy. However, it appears that calculational deficiencies (minimal basis sets) are not responsible for its appearance. Namely, the use of the extended basis set (6-31G) does not change this angle significantly.

The ' transition state ' for the optimum approach of the peroxy-acid to acetylene in the framework of the 1,1-addition mechanism [structure (5)] is calculated to lie 15.3 and 11.8 kcal mol^{-1} (1 cal = 4.184 J) above the optimized geometry of reactants by using STO-4G and 6-31G basis sets, respectively. No experimental data are available to test these results.

The optimized geometry of the ' transition state ' for the 1,3-dipolar addition mechanism, represented as structure (6), has a slightly lower energy than that of (5). Again, electrons are transferred from acetylene to peroxy-acid suggesting the predominance of charge-transfer interactions in this type of reaction. If the finding of C–C bond distance (1.1839 Å) in the acetylenic part of (6) is real, it would again suggest an 'early ' transition state.

As expected from the literature data,[6] the minimal basis sets are unsatisfactory for treating oxiren. By using the 6-31G basis set, the reaction was found to be exothermic by 1.6 kcal mol^{-1}, and an exothermicity of 4.9 kcal mol^{-1} was found by employing the geometry parameters reported by Dykstra.[6c]

Further Oxidation of Oxiren with Peroxyformic Acid.— In order to test the hypothesis of further oxidation of oxiren to 2,4-dioxabicyclo[1.1.0]butane with peroxy-acids, we have investigated the approach of the peroxy-acid to oxiren as well as the structure of the bicyclo-derivative. Although the search of plausible directions of peroxy-acid approach to oxiren was not as exhaustive as that in the study of the first step of the reaction (peroxy-acid + acetylene), it nevertheless appears that the symmetrical attack of peroxyformic acid, analogous to that shown in structure (1), is energetically most favourable [R(C=C) = 1.276 Å; H–$\hat{C}$–C = 180°; R = 3.747 Å; α = 225°; equilibrium energy = −412.550 39 hartrees (STO-4G)].

The planar equilibrium geometry (complete optimization) of 2,4-dioxabicyclo[1.1.0]butane is together with

Table 2

The net atomic charges ($\times 10^{-3}$e) [a]

	(1)	(5)		(6)	HCO_3H		C_2H_2	
Atom	STO-4G	STO-4G	6-31G	STO-4G	STO-4G	6-31G	STO-4G	6-31G
C(1)	−113.16	−105.81	−252.44	−123.58			−110.41	−326.17
C(2)	−113.16	−122.48	−320.91	−106.09			−110.41	−326.17
H(3)	114.68	116.76	287.49	113.07			110.41	326.17
H(4)	114.68	116.45	297.17	117.29			110.41	326 17
H(5)	235.52	235.10	508.22		228.04	476.91		
O(6)	−170.10	−175.49	−397.64	−173.69	−175.00	−379.57		
O(7)	−157.39	−155.58	−400.06	−151.87	−151.64	−389.18		
C(8)	247.87	248.19	585.58	252.67	254.57	587.78		
O(9)	−259.78	−258.41	−560.41	−260.06	−255.89	−549.95		
H(10)	100.85	101.27	253.00	100.92	99.93	254.00		

[a] The term net atomic charge is defined as $Z - n$(STO-4G or 6-31G), where Z is the atomic number and n is the net electronic density of an atom.

the Mulliken population analysis shown in Figure 3. The relatively large bond distance between both bridgehead carbons (1.876 Å) as well as the corresponding negative overlap population indicate clearly an antibonding interaction between both atoms. We conclude, therefore, that such a molecule cannot exist. However, we have not considered the possibility of singlet or triplet diradical states of this molecule.

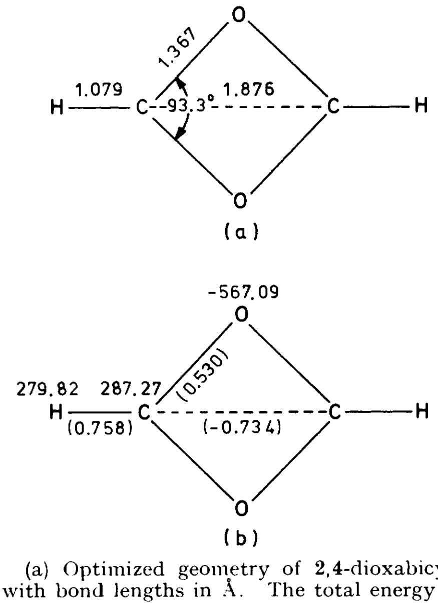


FIGURE 3 (a) Optimized geometry of 2,4-dioxabicyclo[1.1.0]-butane with bond lengths in Å. The total energy calculated with the STO-4G basis set is $-225.085\,70$ hartrees. The 6-31G basis set reduces this value to $-226.285\,60$ hartrees. (b) The net atomic charges ($\times\ 10^{-3}e$) and the total overlap populations (in parentheses) obtained by using the 6-31G basis set

Conclusions.—Although a complete exploration of the energy surface for the reaction of peroxy-acid with acetylene is necessary before one can claim to have shown computationally the detailed mechanistic features of this reaction, we nevertheless believe that our results allow some tentative conclusions.

As in the case of the epoxidation of ethylene, unsymmetrical approaches of the peroxy-acid to acetylene [structures (5) and (6)] are energetically more favourable than a symmetrical one [structure (1)]. The 1,3-dipolar addition of peroxyformic acid to acetylene appears to be slightly preferred over the 1,1-addition [structure (5)]. The approach of the ' electrophilic ' peroxy-acid seems to be dominated by charge-transfer interaction.

The unsymmetrical approach of the peroxy-acid indicated by the present study is in accordance with the experimental observation of the importance of σ^+ contributions to the Hammett correlation in the oxidation of *para*-substituted phenylacetylenes with peroxybenzoic acid ($\rho = -1.04$ with σ^+),[5] indicating the accumulation of a partial positive charge on one of the carbon atoms in the acetylenic part of an open or unsymmetrically partially bridged transition state. For the purposes of the 1,1-addition mechanism, peroxy-acids could thus be regarded as class B reagents in their reactions toward unsaturated C–C bonds, according to a recent classification of electrophiles.[18]

Oxidation of oxiren, if it proceeds at all, does not yield the corresponding dioxabicyclo-derivative. We found that 2,4-dioxabicyclo[1.1.0]butane cannot exist. Nevertheless, the involvement of diradical intermediates in this reaction cannot be excluded.

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