LBL-12756
Preprint c.2

NRCC NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY

DOCUMENTS

Submitted to the Journal of Chemical Physics

THEORETICAL STUDY OF ELECTROPHILIC ADDITION: $O(^3P) + C_2H_4$

M. Dupuis, J.J. Wendoloski, T. Takada, and
W.A. Lester, Jr.

May 1981

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA

LBL-12756 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48 and for the National Science Foundation under Interagency Agreement CHE-7721305

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-12756

To be submitted to Journal of Chemical Physics

THEORETICAL STUDY OF ELECTROPHILIC ADDITION: $O(^3P) + C_2H_4$

M. Dupuis, J. J. Wendoloski, T. Takada and W. A. Lester, Jr.

National Resource of Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48 and by the National Science Foundation under Grant No. CHE-7721305.

This manuscript was printed from originals provided by the authors.

THEORETICAL STUDY OF ELECTROPHILIC ADDITION: $O(^3P) + C_2H_4$

M. Dupuis, J. J. Wendoloski, T. Takada, and W. A. Lester, Jr.

National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract: Ab Initio Hartree-Fock (HF) and Multiconfiguration Hartree-Fock (MCHF) calculations have been carried out to characterize the reactants, transition state, and products of the electrophilic addition of $O(^3P)$ to the π bond of ethylene. The results show that the diradical product CH_2CH_2O is stable with respect to the reactants. The transition state has C_s symmetry, not C_{2v}, with the oxygen atom localized on one of the two double-bond C atoms.

I. Introduction

The reaction of triplet oxygen atoms with olefins has long been assumed to proceed through an electrophilic addition of the oxygen to the π bond to form a diradical intermediate of triplet spin.[1] Because of recent experiments[2,3,4] challenging the dominance of the addition mechanism, there is a need for an accurate characterization of the addition reaction mechanism by i) establishing the nature of the diradical, and its stability with respect to redissociation into $O + C_2H_4$; and ii) determining the activation energy and the structure of the transition state of the addition reaction.

Several studies of the diradical, all using the spin unrestricted Hartree-Fock (UHF) formalism, have been reported previously. Strausz et al.,[5] using a double zeta quality basis set and partially optimized structures, reported an unrealistic high barrier to C-C rotation in CH_2-CH_2-O. Bader et al.[6] using an extended basis set including polarization functions, and partially optimized structures found a high barrier to C-C rotation of 5 kcal/mol, and failed to find a diradical structure stable to redissociation. Yamaguchi et al.[7] used a double zeta quality basis set, and fully optimized the structure of the diradical. The calculated barrier to internal rotation about the C-C bond was found to be small, less than 1.0 kcal/mol, thus substantiating the non-stereospecifity of the addition reaction. Their computed structure corresponds to a local minimum on the energy surface, although it is ~6 kcal/mol above the reactants energy. The enthalpy of diradical formation reported by Pudzianowski et al.[8] using the MINDO/3 method[9] is unrealistically too large.[10]

Two characterizations of the addition reaction path have been reported. Bader et al.[6] showed that the reaction path of triplet spin corresponds to an asymmetric approach of the reactants to form the diradical. However, they invoked an intersystem crossing at an energy 36 kcal/mol above the reactants energy to reach the reaction products. This result is in contradiction with the experimentally determined activation energy (~1 kcal/mol). Pudzianowski et al.[8] suggested a symmetric transition state leading to an unsymmetrical diradical product from MINDO/3 calculations. However, in a more recent study using the MNDO method, they obtained an asymmetric transition state.[11]

Here we report ab initio Hartree-Fock (HF) and multiconfiguration Hartree-Fock (MCHF) calculations of the structure of the transition state and of the diradical. The computational method used throughout this study is briefly described in section II. The structure of the diradical calculated with a double zeta quality plus polarization basis set and spin restricted HF wavefunctions is described in section III. The structure of the transition state of the electrophilic addition, calculated with a double zeta quality basis set and a MCHF wavefunction, is presented in section IV. Because the experimental activation energy for the reaction is ~1 kcal/mole, we did not attempt to calculate it accurately. Instead we focused our effort on defining a wavefunction which describes the addition mechanism in a qualitatively reliable way.

II. Computational Method

All the structures reported in the present study correspond to fully optimized geometries obtained with the gradient method using spin-restricted Hartree-Fock (HF) and multiconfiguration (MCHF) wavefunctions. We used Pople's STO-3G,[12] Poples' double zeta quality 3-21G[13] and Dunning's double zeta plus polarization (DZP) basis sets.[14] The latter consisted of his (9s,5p)/(3s,2p) basis set augmented with polarization functions ($\alpha_d^C = 0.75$, $\alpha_d^O = 0.85$, $\alpha_p^H = 1.0$). The calculations were carried out with the HONDO program,[15] which includes a Newton-Raphson orbital optimization procedure for MCHF calculations,[16] and the GUCA-CI program developed by Brooks[17] for configuration interaction (CI) calculations.

III. Open Ring Oxirane Diradical CH_2CH_2O

The structure and electronic states of the diradical CH_2CH_2O have been extensively discussed by Yamaguchi et al.[7] For completeness we reproduce in Fig. 1 the structures and the labels described in Ref. 7. The labels $\sigma\sigma$, $\sigma\pi$, $\pi\sigma$, and $\pi\pi$ describe the orientation of the unpaired electrons on the terminal carbon and on the oxygen: the first character (σ or π) refers to the C unpaired electron, the second character (σ or π) refers to the O unpaired electron; σ means the unpaired electron orbital is in the CCO symmetry plane, π means it is out-of-plane.

The energies of the oxygen atom and ethylene molecule are given in Table I. The energies of the singlet and triplet manifolds are given in Table II, along with the relative energies with respect to the reactants

Table I. HF energies[a] of oxygen atom and ethylene C_2H_4.

	STO-3G[b]	3-21G	DZP
$C_2H_4(^1A_1)$	-77.073955	-77.600990	-78.050702
$O(^3P)$	-73.804150	-74.391782	-74.798857
$O(^3A'')$[c]	-73.804150	-74.392511	-74.800589

[a]Energies in atomic units.

[b]See text for basis sets. Geometries are optimized for the various basis sets.

[c]C_s symmetry only.

Table II. HF total and relative energies[a] of CH_2CH_2O radical electronic states.

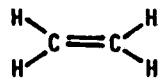
		STO-3G[b]		3-21G		DZP	
$O + C_2H_4$[c]		-150.878105	(0.0)	-151.993501	(0.0)	-152.851293	(0.0)
CH_2CH_2O	$^3A''\sigma\pi$	-150.896204	(-11.4)	-151.979038	(+8.6)	-152.853860	(-4.4)
	$^3A'\sigma\sigma$	-150.894448	(-10.3)	-151.976048	(+10.5)	-152.855634	(-2.7)
	$^3A'\pi\pi$	-150.893593	(-9.7)	-151.979216	(+8.5)	-152.858350	(-4.4)
	$^3A''\pi\sigma$	-150.893370	(-9.6)	-151.976841	(+10.0)	-152.856746	(-3.4)
	$^1A''\sigma\pi$	-150.893595	(-9.7)	-151.975920	(+10.6)	-152.855744	(-2.8)
	$^1A'\sigma\sigma$	-150.890405	(-7.7)	-151.971750	(+13.2)	-152.851495	(-0.1)
	$^1A'\pi\pi$	-150.892771	(-9.2)	-151.977976	(+9.3)	-152.856833	(-3.5)
	$^1A''\pi\sigma$	-150.890830	(-8.0)	-151.974270	(+11.6)	-152.853878	(-1.6)

[a]Energies in atomic units; relative energies in kcal/mol in parentheses.

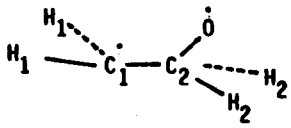
[b]See text for basis sets. Geometries are optimized for the various basis sets.

[c]The energies of $O(^3A'')$ in C_s symmetry are used (see Table I).

Table III. HF geometries[a] of C_2H_4 and CH_2CH_2O radical states (DZP basis set)[b].

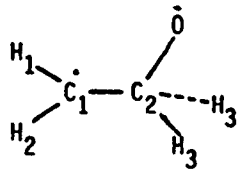


	$^1A_1$
	-78.050702
R(CC)	1.325
R(CH)	1.076
<(HCC)	121.6



	$^3A''\sigma\pi$	$^3A'\sigma\sigma$	$^1A''\sigma\pi$	$^1A'\sigma\sigma$
	-152.858386	-152.855634	-152.855744	-152.851495
$R(C_1C_2)$[c]	1.499	1.504	1.506	1.509
$R(C_2O)$	1.399	1.403	1.396	1.407
$R(C_1H_1)$	1.075	1.074	1.075	1.074
$R(C_2H_2)$	1.087	1.086	1.087	1.086
$<(C_1C_2O)$	113.5	110.6	114.1	110.9
$<(H_1C_1C_2)$	119.2	119.6	119.0	119.7
$<(H_2C_2C_1)$	111.5	109.5	111.2	109.7
$\delta(H_1C_1C_2O)$	78.3	81.5	77.9	79.8
$\theta(C_1C_2H_2,C_1C_2O)$	120.3	120.1	120.6	120.1
$\alpha(H_1C_1H_1,C_1C_2)$	20.0	14.6	20.7	17.2

Table III. (continued)

	$^3A'_{\pi\pi}$	$^3A''_{\pi\sigma}$	$^1A'_{\pi\pi}$	$^1A'_{\pi\sigma}$
	-152.858350	-152.856746	-152.856833	-152.853878
$R(C_1C_2)$[d]	1.498	1.503	1.502	1.502
$R(C_2O)$	1.390	1.390	1.395	1.401
$R(C_1H_1)$	1.072	1.072	1.072	1.072
$R(C_1H_2)$	1.073	1.072	1.074	1.073
$R(C_2H_3)$	1.089	1.088	1.088	1.088
$<(C_1C_2O)$	113.3	108.6	113.2	109.1
$<(H_1C_1C_2)$	120.0	121.8	120.0	121.6
$<(H_2C_1C_2)$	120.0	118.5	120.0	118.7
$<(C_1C_2H_3)$	11.4	109.9	111.3	110.1
$\theta(C_1C_2H_3,C_1C_2O)$	120.8	120.3	120.6	120.3

[a]Bond lengths in angstrom, angles in degrees, energies in atomic units.

[b]See text for basis set description.

[c]The (C_1C_2O) plane is the plane of symmetry. δ is the dihedral angle between the (C_1C_2O) and $(H_1C_1C_2)$ planes. θ is the dihedral angle between the (C_1C_2O) and $(C_1C_2H_2)$ planes. α is the out-of-plane angle defined by the angle of C_1C_2 with the $H_1C_1H_1$ plane.

[d]The C_1C_2O plane is the plane of symmetry. θ is the dihedral angle between the (C_1C_2O) and $(C_1C_2H_3)$ planes.

for the different energy ordering. Furthermore they obtained a smaller CCO angle in the $^1A'(\sigma\sigma)$ state. Our results do not support their finding. Overall, for the triplet and singlet manifolds the oxygen σ unpaired electron interacts more with the terminal methylene radical center than the π electron, resulting in a smaller CCO angle (~109.5°) in the $\sigma\sigma$ and $\pi\sigma$ states and a larger CCO angle (~113°) in the $\sigma\pi$ and $\pi\pi$ states. The out-of-plane bending angles of the methylene radical center in the $\sigma\sigma$ and $\sigma\pi$ states is found to be between 14.5° and 20.7°, slightly larger than the values of Yamaguchi et al.[7]

The diradical structures show some striking similarities to the ethyl radical structure.[19] The CH bonds of the methylene radical center are ethylenic (~1.074 Å), i.e., shorter than the CH bond on the central carbon (~1.087 Å). There is an hyperconjugative interaction of the carbon unpaired electron with the CH bonds of the central carbon, which are consistently longer in the $\pi\sigma$ and $\pi\pi$ states than in the corresponding $\sigma\sigma$ and $\sigma\pi$ states. The out-of-plane bending angles for the $\sigma\sigma$ and $\sigma\pi$ states are between 14° and 21° and much larger than those in the ethyl radical (6°) indicating a strong interaction of the two localized unpaired electrons.

These differences are confirmed by the vibrational analysis performed on the $^3A''(\sigma\pi)$ state (HF wavefunction and DZP basis set) and shown in Table IV. The lowest frequency vibrational mode (316 cm^{-1}) corresponds to the internal rotation of the CH_2-radical center about the C-C bond. It is in qualitative agreement with the small energy

Table IV. Vibrational analysis of $^3A''(\sigma\pi)$ CH_2CH_2O diradical.

mode	$\nu(cm^{-1})$	mode	$\nu(cm^{-1})$
1. $\dot{C}H_2$-C rotation	316	9. CH bend, twist, rock	1491
2. CCO bend	443	10. CH bend, twist, rock	1572
3. $\dot{C}H_2$ - pyramidal bend	707	11. CH bend, twist rock	1608
4. -CH- bend	810	12. $-CH_2-$ symmetric stretch	3215
5. C-C-O symmetric stretch	1083	13. $-CH_2-$ asymmetric stretch	3261
6. C-C-O asymmetric stretch	1163	14. $\dot{C}H_2-$ symmetric stretch	3325
7. CH bend, twist, rock	1193	15. $\dot{C}H_2-$ asymmetric stretch	3435
8. CH bend, twist, rock	1396		

difference between the $^3A''(\sigma\pi)$ and $^3A'(\pi\pi)$ states. The pyramidal bending mode of the CH_2 radical group has a frequency of 707 cm^{-1}, larger than the frequency of this mode in the ethyl radical[19] (540 cm^{-1}). This finding is in accord with the larger bending angle (20.0°) in the CH_2CH_2O compared to ethyl (6°). The low frequency (443 cm^{-1}) of the CCO bending mode indicates a flat bending potential, and low barrier to ring closure. The CH bonds on the radical center are ethylenic, shorter than the CH bonds on the central carbon, a characteristic reflected in the stretching frequencies (3325, 3425 cm^{-1} for CH_2 and 3215, 3251 cm^{-1} for $-CH_2-$).

IV. The $O(^3A'') + C_2H_4(^1A_1)$ Transition State

Cvetanovic[1] attributed the attractive interaction energy in the oxygen atom plus olefin addition reaction to a partial charge transfer from the olefin to the attacking oxygen atom, the initial electrostatic repulsion being responsible for the existence of a reaction energy barrier. Bader et al.[6] described the reaction process as a spin uncoupling mechanism including i) an initial uncoupling of the olefin π-bonding electron density, ii) a recoupling of the central carbon electron density to the oxygen density, and iii) a localization of the unpaired electron. Thus they argue that the decrease in carbon-carbon π binding occurs simultaneously with an increase in the carbon-oxygen binding.

A schematic orbital representation of the addition reaction is shown in Fig. 2. During the course of the reaction the system maintains the C-C-O plane as a plane of symmetry. The original C=C π bond and its antibonding counterpart π^* have a' symmetry. The unpaired electrons on the oxygen atom are in orbitals of a' and a" symmetry. The a" electron on the oxygen atom plays a passive role during the reaction. At the beginning of the reaction a three-active-electron wavefunction can be written $p_O\alpha(p_{C1} + p_{C2})(\alpha\beta-\beta\alpha)/\sqrt{2}$, where p_O is the in-plane oxygen orbital, p_{C1} and p_{C2} are the out-of-plane orbitals of C_1 and C_2. As the reaction proceeds the π electrons uncouple, the hydrogens on the central carbon C_2 are pushed back and C_2 acquires an approximate sp^3 hybridization. The "unpaired" electron on C_2 recouples with the oxygen p electron to form a σ bond. At the end of the reaction the wavefunction can be written $p_{C1}\alpha(sp_{C2}{}^3 + p_O)(\alpha\beta-\beta\alpha/\sqrt{2})$, where $sp_{C2}{}^3$ represents the hybrid orbital of C_2. This qualitative wavefunction description shows the crucial role of the $p\pi$ orbitals on the carbon atom and the in-plane p orbital of the oxygen atom unpaired electron. Within this set of orbitals the electrons can be described by the following coupling scheme: $(p_{C1}-p_{C2})$ coupled singlet for the reactants and $(sp_{C2}{}^3-p_O)$ coupled singlet for the diradical.

The multiconfiguration wavefunction, obtained by disturbing the three active electrons in all possible ways among the three active a' orbitals, contains the electron recoupling configurations which play a key role in the transition state description. For the $^3A''$ state of interest, the MCHF wavefunction includes 9 configuration state functions.

The total energies, relative energies, and geometries (see Fig. 3) of the reactants, transition state, and products of the addition reaction are given in Tables V and VI for the STO-3G and 3-21G basis sets. From Table V one sees that the electron correlation correction from the MCHF wavefunction results in a less stable diradical for both the STO-3G and the 3-21G basis sets. The HF results shown in Table II give an energy difference between the diradical and the reactants $O(^3A'') + C_2H_4(^1A_1)$ of -11.4 kcal/mol with the STO-3G basis, an +8.6 kcal/mol with the 3-21G basis. The corresponding MCHF energies are -1.7 kcal/mol with the STO-3G basis and +10.5 kcal/mole for the 3-21G basis. These small energy differences imply a "loose" transition state which is found ~16 kcal/mol above the reactants for both basis sets. The energy barrier is small, and it is likely that a better basis set and a more extended treatment of electronic correlation effects would bring this value very close to the experimental activation energy (~1 kcal/mol). The transition state geometries reported in Table V for the two sets are similar, with an elongated C-O internuclear distance. The angle of approach of the oxygen atom is ~107° with respect to the C-C bond for both basis sets. At the transition state the hydrogen atoms attached to the terminal carbon are ~8° out of the ethylene plane, and the hydrogen atoms on C_2 are ~28° out of the plane. The out-of-plane angle of the methylene group in the diradical is sensitive to the basis set (27.4° for the STO-3G basis, and 12.8° for

Table V. MCHF total[a] and relative energies[b] of reactants, transition state and products of the $O(^3P) + C_2H_4(^1A_1)$ reaction.

	STO-3G		3-21G	
$O(^3A'') + C_2H_4(^1A_1)$	-150.920970	(0.0)	-152.023549	(0.0)
CH_2-CH_2-----$O(^3A'')$	-150.895829	(+15.8)	-151.997108	(+16.6)
CH_2CH_2O $(^3A'')$	-150.923606	(+1.7)	-152.006776	(+10.5)

[a]Energies in atomic units.

[b]Relative energies in parentheses in kcal/mol.

Table VI. MCHF geometries[a] of reactants, transition state, and products of the $O(^3P) + C_2H_4(^1A)$ reaction.

	Reactants		Transition State		Product	
	STO-3G	3-21G	STO-3G	3-21G	STO-3G	3-21G
$R(C_2O)$	∞	∞	1.913	1.873	1.510	1.533
$<(C_1C_2O)$			107.8	107.4	112.7	111.9
$R(C_1C_2)$	1.341	1.336	1.395	1.399	1.513	1.482
$R(C_1H_1)$	1.081	1.074	1.081	1.072	1.083	1.071
$R(C_2H_2)$	1.081	1.074	1.084	1.074	1.093	1.081
$<(C_2C_1H_1)$	121.9	121.8	121.0	121.0	118.1	120.1
$<(C_1C_2H_2)$	121.9	121.8	118.6	118.7	111.3	113.0
$\delta(H_1C_1C_2O)$[b]	90.0	90.0	84.2	85.2	73.9	82.8
$\theta(C_1C_2H_2,C_1C_2O)$	90.0	90.0	106.7	106.7	119.4	118.0
α	0.0	0.0	9.5	7.9	27.4	12.8
β	0.0	0.0	27.7	27.8	51.5	47.6

[a]Bond lengths in angstroms, angles in degrees. See Fig. 3 for definition.

[b]The (C_1C_2O) plane is the plane of symmetry. δ is the dihedral angle between the (C_1C_2O) and $(H_1C_1C_2)$ planes. θ is the dihedral angle between the (C_1C_2O) plane and the $(C_1C_2H_2)$ planes. See Fig. 3 for definition of α and β angles.

the 3-21G basis). The bending angle for the hydrogens on C_2 is about 48° in the diradical. A vibrational analysis of the STO-3G transition state structure yielded only one negative eigenvalue (887 cm^{-1}) corresponding to an attack of the oxygen atom on the π bond as the hydrogen atoms on the central carbon are pushed backwards.The next lowest eigenvalue is positive (290 cm^{-1}) corresponding to a CCO bending motion, clearly showing that the path of attack corresponds to a valley on the potential energy surface.

The natural orbitals (NO) (Fig. 4) of the MCHF wavefunction and their occupation numbers (Table VII) reveal some interesting features. For the reactants, the NO's are the π bonding orbital (occupation = 1.90), the oxygen unpaired electron orbital (occupation = 1.00), and the π^* anti-bonding orbital (occupation = 0.10). The NO's of the transition state show the buildup of the unpaired electron on the methylene carbon. In the first transition state NO (occupation = 1.83) the electron population is shifted toward C_2 and the oxygen atom. The terminal carbon has acquired a radical character in the second NO (occupation 1.00). For the products, the first NO corresponds to a CO bonding orbital (occupation = 1.96), while the second NO is the orbital of the unpaired electron on the methylene carbon. The change in character of the NO's reflects the crucial role of the configuration mixing in the description of the addition reaction.

Table VII. Occupation numbers and selected populations of the active MCHF natural orbitals[a] for the reaction $O(^3P) + C_2H_4$.

			ϕ_1	ϕ_2	ϕ_3
Reactants	occupation		1.90	1.00	0.10
	population	C_1	0.95	0.00	0.05
		C_2	0.95	0.00	0.05
		O	0.00	1.00	0.00
Transition state	occupation		1.87	1.00	0.13
	population	C_1	0.40	0.54	0.03
		C_2	0.76	0.00	0.06
		O	0.66	0.44	0.03
Products	occupation		1.96	1.00	0.04
	population	C_1	0.04	0.92	0.00
		C_2	0.85	0.00	0.02
		O	1.21	0.05	0.01

[a]See Fig. 4 for orbital descriptions.

Conclusions

Through the use of a MCHF wavefunction we have shown that the transition state for the electrophilic addition of $O(^3P)$ to ethylene is asymmetric. We feel that improvements in basis set and electron correlation description are unlikely to change the qualitative conclusions reached in this work regarding the nature and structure of the transition state. Foremost, there is the finding that during the addition process the electrons involved in bond breaking and bond formation undergo a spin uncoupling mechanism comparable to a quasi excitation from a π^2 configuration to a $^3\pi$-π^* configuration, followed by a spin recoupling with the attacking electron. As first shown by Bader et al.,[5] the asymmetric approach is found to correspond to the most favorable nuclear arrangement for minimizing electron repulsion.

The asymmetry of the transition state is in accord with the observed pronounced orienting effect in the addition in which the oxygen atom attacks the less substituted carbon atom of the olefin double bond. Several effects compete in this process. On the one hand, the alkyl substituents donate electron density to the substituted carbon which the oxygen atom might be expected to preferentially attack. Steric hindrance, however, makes an attack on the substituted carbon more difficult, and favors the attack on the less substituted carbon. Another factor which plays a role is the radical stabilization effect. Tertiary radicals are more stable than secondary radicals, and secondary radicals more stable than primary radicals. In accord with this result, the radical center created during the course of the reaction is

stabilized by substituents. Thus, we conclude that steric effects and radical stabilization are responsible for the attack of the oxygen atom on the less substituted carbon.

Acknowledgments

The authors gratefully acknowledge A. T. Pudzianowski and G. H. Loew for making their findings available prior to publication, and A. T. Pudzianowski for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract no. W-7405-ENG-48 and by the National Science Foundation under Grant No. CHE-7721305.

References

1. R. J. Cvetanovic, Adv. Photochem. 1, 115 (1963).
2. Y. T. Lee, Lecture presented at the 14th Informal Conference on Photochemistry, Newport Beach, California, April 1980.
3. H. R. Wendt, H. Kneppe, H. E. Hunziker, submitted to J. Chem. Phys.
4. K. Kleinermans, A. C. Luntz, submitted to J. Chem. Phys.
5. O. P. Strausz, R. K. Gasari, G. R. Demare, and I. G. Czismadia, Chem. Phys. Lett. 62, 339 (1979).
6. R. F. W. Bader, M. E. Stephens, R. A. Gangi, Can. J. Chem. 55, 2755 (1977).
7. K. Yamaguchi, S. Yabushita, T. Fueno, S. Kato, K. Morokuma, Chem. Phys. Lett. 70, 27 (1980).
8. A. T. Pudzianowski, G. H. Loew, J. Am. Chem. Soc. 102, 5443 (1980).
9. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc. 97, 1285 (1975).
10. L. B. Harding, submitted to J. Am. Chem. Soc.
11. A. T. Pudzianowski, G. H. Loew, submitted to J. Am. Chem. Soc.
12. W. J. Hehre, R. F. Stewart, J. A. Pople, J. Am. Chem. Soc. 51, 2657 (1969).
13. J. S. Binkley, J. A. Pople, W. J. Hehre, J. Am. Chem. Soc. 102, 939 (1980).
14. T. H. Dunning, Jr. and P. J. Hay, "Modern Theoretical Chemistry," vol. 2, H. F. Schaefer III, Ed. (Plenum Press, New York, 1976).

15. M. Dupuis, J. Rys, H. F. King, J. Chem. Phys. 65, 111 (1976).
M. Dupuis, J. J. Wendoloski, D. Spangler, Nat. Resour. Comput. Chem. Software Cat. vol. 1, prog no. QGØ1, (1980).

16. L. Yaffe, W. A. Goddard III, Phys. Ref. A13, 1682 (1985).

17. B. R. Brooks, Ph.D. Thesis, University of California, Berkeley.

18. M. Dupuis, J. J. Wendoloski, W. A. Lester, Jr., to be published.

19. J. Pacansky, M. Dupuis, J. Chem. Phys. 68, 4276 (1978).

Table Captions

Table I. HF energies[a] of oxygen atom and ethylene C_2H_4

a. Energies in atomic units.

b. See text for basis sets. Geometries are optimized for the various basis sets.

Table II. HF total and relative energies[a] of CH_2CH_2O radical electronic states.

a. Energies in atomic units; relative energies in kcal/mole in parentheses.

b. See text for basis sets. Geometries are optimized for the various basis sets.

Table III. HF geometries[a] of C_2H_4 and CH_2CH_2O radical states (DZP basis sets).[b]

a. Bond lengths in angstroms, angles in degrees, energies in atomic units.

b. See text for basis set description.

Table IV. Vibrational analysis of $^3A''(\sigma\pi)$ CH_2CH_2O radical.

Table V. MCHF total[a] and relative energies[b] of reactants, transition state and products of the $O(^3P) + C_2H_4$ reaction.

a. Energies in atomic units.

b. Relative energies in kcal/mole in parentheses.

Table VI. MCHF geometries[a] of reactants, transition state, and products of the $O(^3P) + C_2H_4$ reaction.

a. Bond lengths in angstroms, angles in degrees.

Table VII. Occupation numbers and selected populations of the active MCHF natural orbitals[a] for the reaction $O(^3P) + C_2H_4$.

a. See Fig. 4 for orbital description.

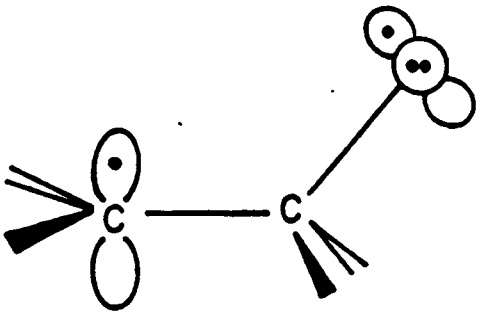
Figure Captions

Fig. 1. The electronic states of the CH_2CH_2O diradical.

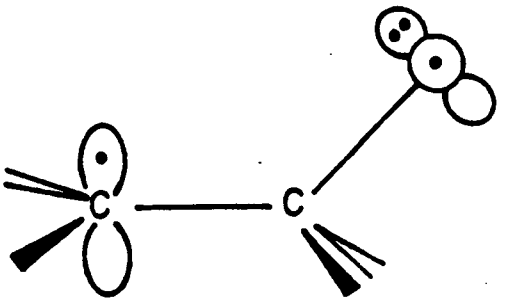
Fig. 2. Molecular orbital description of the transition state for the reaction $O(^3P) + C_2H_4(^1A_1)$.

Fig. 3. Structure of the CH_2CH_2O system.

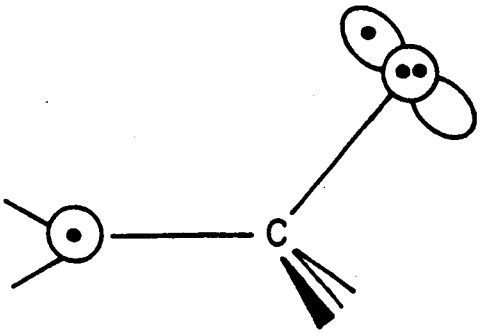
Fig. 4. Active MCHF natural orbitals for the $O(^3P) + C_2H_4$ reaction.



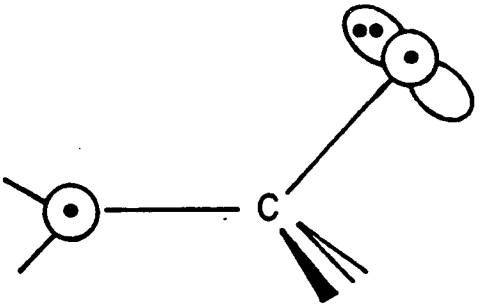
$^{1,3}A'$ $(\sigma\sigma)$



$^{1,3}A''$ $(\sigma\pi)$



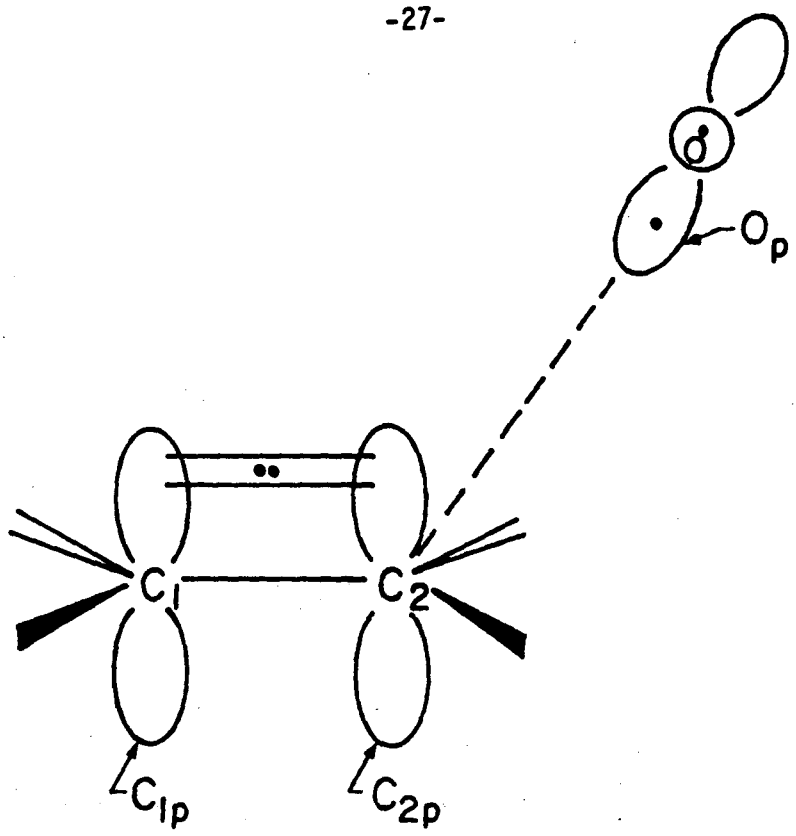
$^{1,3}A''$ (π,σ)



$^{1,3}A'$ (π,π)

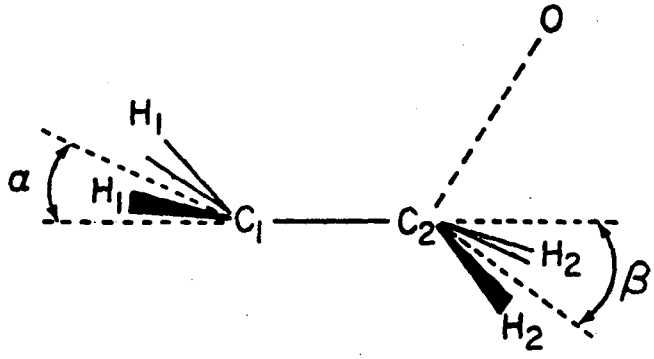
XBL816-2305

Fig. 1.



XBL 816-2307

Fig. 2.



XBL 816-2308

Fig. 3.

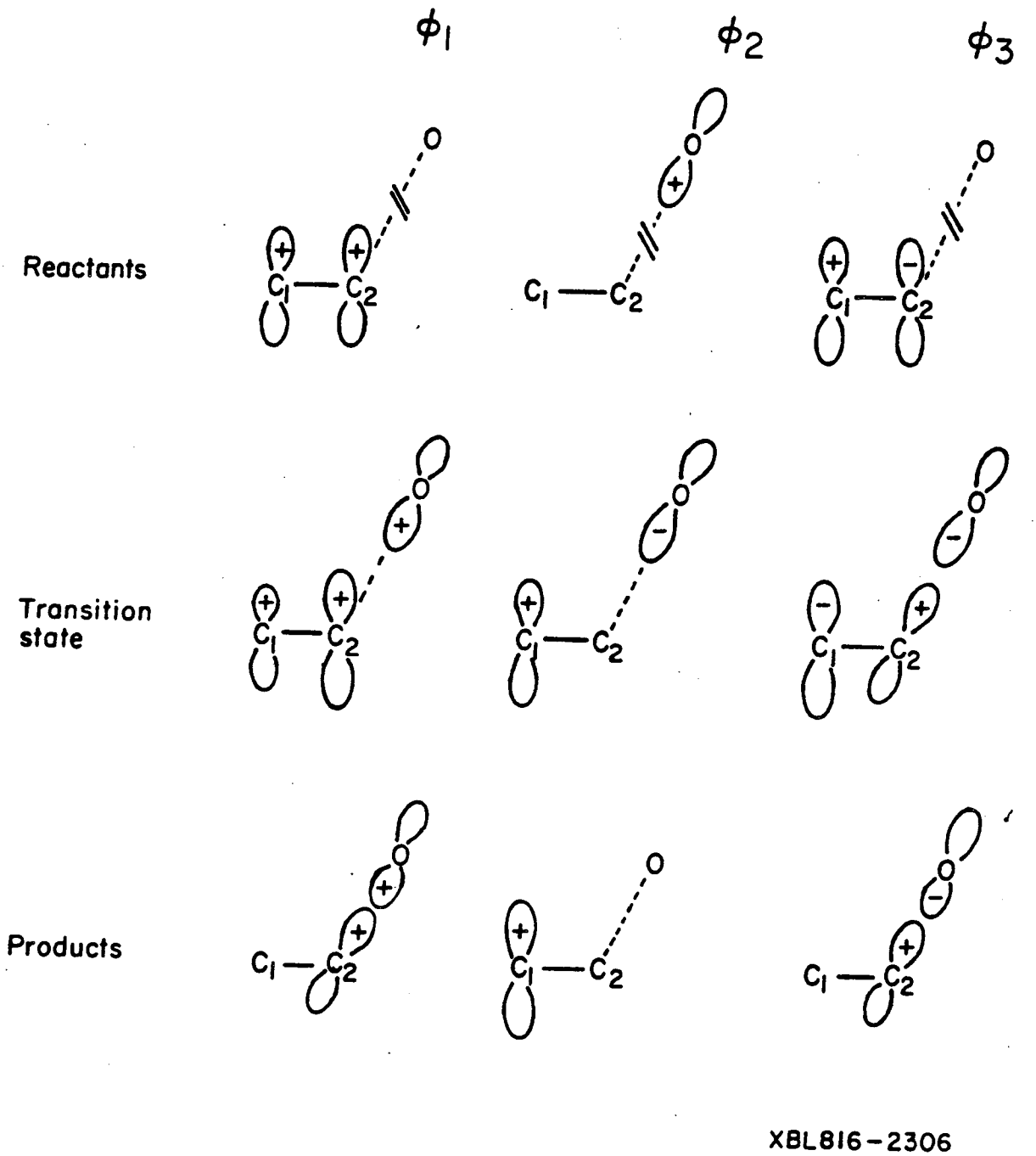

ϕ_1
ϕ_2
ϕ_3
Reactants
Transition state
Products
C_1
C_2
O
XBL816-2306

Fig. 4.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720