Potential Energy Surfaces for Atomic Oxygen Reactions:
Formation of Singlet and Triplet Biradicals as Primary
Reaction Products with Unsaturated Organic Molecules

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ABSTRACT

The experimental study of the interaction of atomic oxygen with organic polymer films under *LEO* conditions has been hampered by the inability to conduct detailed experiments *in situ*. As a result, studies of the mechanism of oxygen atom reactions have relied on laboratory O-atom sources that do not fully reproduce the orbital environment. For example, it is well established that only ground electronic state oxygen atoms are present at *LEO*, yet most ground-based oxygen sources are known to produce singlet oxygen atoms and molecules and ions in addition to $O(^3P)$. Engineers should not rely on such facilities unless it can be demonstrated either that these different oxygen species are inert or that they react in the same fashion as ground state atoms.

Ab initio quantum chemical calculations carried out at NASA Ames and elsewhere have been aimed at elucidating the biradical intermediates formed during the electrophilic addition of ground and excited-state oxygen atoms to carbon-carbon double bonds in small olefins and aromatic molecules. These biradicals are critical intermediates in any possible insertion, addition and elimination reaction mechanisms. Through these calculations, we will be able to comment on the relative importance of these pathways for $O(^3P)$ and $O(^1D)$ reactions. The reactions of oxygen atoms with ethylene and benzene will be used to illustrate the important features of the mechanisms of atomic oxygen reaction with unsaturated organic compounds and polymeric materials.

I. INTRODUCTION

The kinetics and mechanisms of the chemical reactions of oxygen atoms with organic molecules have been the subject of intensive study for more than thirty years. Most of these investigations have been carried out in the gas phase as the major impetus for this work has come from the combustion and atmospheric photochemistry research communities. Cvetanovic and Singleton[1] have recently reviewed this work for the case of O-atom olefin reactions. Companion studies have been carried out by Klein and Scherr[2] in low temperature glasses. These studies have been fraught with difficulties, as it is not an easy task to generated a clean, controlled and calibrated source of oxygen atoms. More recently, molecular beam studies of $O(^3P)$ reactions with organic species under single-collision conditions have provided a detailed look at the primary processes in these complicated reactions[3-6]. A comprehensive reaction mechanism must be capable of describing these single-collision, gas phase and condensed phase experiments.

The chemistry of atomic oxygen is made especially interesting by that species' triplet ground electronic state and by the existence of a low-lying excited singlet state[7]. The following general conclusions can be drawn from this large body of work[1,8,9]: $O(^3P)$ **abstracts hydrogen from saturated organic molecules and adds to carbon-carbon double bonds resulting in the formation of carbonyl compounds and epoxides, while $O(^1D)$ tends to form alcohols by inserting into C-H bonds.** These initial products undergo secondary reactions which lead to fragmentation of the reactant molecules. In most cases, the branching ratios for secondary fragmentation products are **statistical**, meaning they are governed by the relative thermodynamic stabilities of the energetically permissible products (or by the relative ease of bond rupture).

Renewed interest in the kinetics and mechanisms of atomic oxygen reactions has been generated during the early flights of the space shuttle by observations that most organic polymeric materials undergo noticeable degradation during exposure to the low Earth orbit (*LEO*) environment[10,11]. The most severe damage was observed on surfaces facing the direction of motion in orbit. In this orientation, both the flux and the kinetic energy of the atmospheric species striking the surface are high ($\approx 10^{15}\mathrm{cm}^{-2}\mathrm{s}^{-1}$ and 5-10 eV). Ground state atomic oxygen is the principal constituent of the residual atmosphere in the 150-250 km altitude range and it seems likely that this species would react readily with most organic materials. Dedicated flight experiments on shuttle flights STS-5 and STS-8 have confirmed these early observations[10], indicating that the degradation is widespread and independent of surface temperature and solar UV/VUV irradiation.

Several laboratory facilities[12] have been constructed in an attempt to simulate the *LEO* environment for kinetic and mechanistic studies and for screening materials proposed for use on the space telescope and space station projects. Unfortunately none of these facilities is capable of completely achieving the desired conditions: a beam of 5 eV $O(^3P)$ atoms of the appropriate flux and without contamination from O_2, O^+, $O(^1D)$ or other reactive species.

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As one purpose of this workshop is to assess the current status of laboratory simulation of the *LEO* environment, it is appropriate to examine the differences in the reaction mechanisms of $O(^3P)$ and $O(^1D)$ with organic compounds. It should be pointed out that very little is known about O atom reactions with polymers(13) and there is no certainty that the same mechanisms apply to the reactions of small molecules and polymers. However, it is likely that the initial steps in the reaction mechanisms are the same in both cases. In the present study we consider the reactions of atomic oxygen atoms with unsaturated organic molecules from a theoretical point of view. We describe a previous computational study of the addition of oxygen to ethylene(14) and present the results of new calculations for the reaction of $O(^3P)$ + benzene. These systems are chosen because of the availability of experimental data and because they have features in common with organic polymers being considered for *LEO* applications such as *KAPTON* (a polyimide film) and structural materials such as PEEK and polysulfone. Some of the questions we will attempt to answer are: "under *LEO* conditions will $O(^3P)$ and $O(^1D)$ react differently?", "are the kinetics affected by the 5 eV O atom energy?", and "how do the degradation rates scale with O-atom flux?".

II. COMPUTATIONAL DETAILS

In recent years, computational chemistry groups at NASA Ames Research Center and elsewhere have been able to capitalize on the availability of supercomputers such as the Cray XMP and have been performing accurate "**first principles**" calculations of the spectroscopic, kinetic and thermodynamic properties of small molecules. These data arise from solutions of the Schrödinger equation which describes the energy and distribution (*wave function*) of a collection of electrons in the field created by the motionless nuclei of the atoms in a molecule(15). By relaxing the locations of the atoms in a series of calculations, molecular equilibrium geometries and saddle points for chemical reactions can be determined. Collisional and spectroscopic properties are obtained by subsequent calculations in which the nuclei are allowed to move, subject to the forces generated by the gradient of the electronic energies.

The calculations reported herein utilize several "standard" aspects of *ab initio* quantum chemistry codes(15). The molecular wavefunction is expanded in a basis of Gaussian functions which represent atomic orbitals and, at the Hartree-Fock or Self-Consistent Field (SCF) level of calculation, each electron experiences only the average field of the remaining electrons in the molecule. SCF calculations give only an approximate picture of the electron density distribution in a molecule. A more accurate description is obtained by allowing each electron to feel the instantaneous influence of all the other electrons. Various computational schemes have been developed to include these effects, two examples of which are the multiconfiguration self-consistent field (MCSCF) and configuration interaction (CI) methods. These effects are generally of critical importance in the study of chemical bond breaking and formation. However, experience has shown that SCF calculations are quite adequate for the determination of geometries for stable molecules

and reaction intermediates.

In the present study we have used all of the above mentioned methods. The calculations were carried out using Dunning's double-ζ atomic orbital basis sets in which 9s and 5p Gaussian functions are contracted to make 4s and 2p orbitals for each carbon and oxygen atom and 5s Gaussians are contracted to 3s orbitals for each hydrogen[16]. The molecular geometries were determined by minimizing the norm of the analytic gradient of the SCF energy using a computer code GRADSCF[17]. At these **stationary** points, the analytic second derivatives of the energy were evaluated to determine whether the computed geometries correspond to local minima or to saddle points[18]. At the SCF geometries, a variation of MCSCF calculation known as the Complete Active Space SCF method (CASSCF) was employed[19]. In these calculations, the oxygen 2p electrons and orbitals and the benzene π electrons and orbitals were included in the "active space" and the interactions between all possible arrangements of those 10 electrons in the 9 orbitals were considered. Finally, contracted CI calculations[20] were performed using the CASSCF orbitals as reference vectors and including single and double excitations from a set of reference configurations comprised of all configurations making important contributions to the CASSCF wavefunction at any of the molecular geometries considered. For O + benzene in C_S symmetry $^3A'$, $^3A''$, $^1A'$ and $^1A''$ states are possible. The sizes of the CASSCF and CCI wavefunctions generated for each of these states are given in Table I.

III. O(^{3}P) + ETHYLENE

The reaction of ground state oxygen atoms with ethylene has been the subject of extensive experimental[1,3-6,8,21-23] and theoretical[14] study. The gas phase kinetics studies demonstrated that O(^{3}P) readily adds to the carbon-carbon double bond, resulting in the formation of a transient **biradical** species which undergoes triplet-singlet interconversion and rearrangement leading to epoxide and aldehyde products. However, molecular beam experiments under single-collision conditions found rapid hydrogen atom elimination follows the biradical formation almost exclusively (4-6,23). The elimination pathway is favored under these conditions because it does not require a change in electron spin. Carbon-carbon bond rupture to form fragmentation products (either formaldehyde and methylene or, after a 1,2-hydrogen shift, formyl and methyl radicals) is possible, but does not seem to occur. Similarly, the rearrangement to form triplet acetaldehyde is not observed, probably because the hydrogen shift involves surmounting a higher energy barrier than does hydrogen elimination. Figure 1 is a schematic energy diagram (taken from ref. 8) which describes these processes.

One of the important results of the theoretical study is that the singlet and triplet biradicals are nearly degenerate and intersystem crossing should occur readily under multiple collision conditions (e. g., bulk gas or condensed phase). Once the system has been converted to the singlet manifold, rearrangement to form ethylene oxide or acetaldehyde can compete with the still-present elimination channel. The addition products are ex-

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tremely stable compared to the biradical (≈ 400 kJ/mol for acetaldehyde), but collisional stabilization is required to prevent their unimolecular fragmentation.

The reactions of $O(^1D)$ can proceed by the same biradical-addition pathway as in the triplet case, or by direct insertion into the C-H bond to form $(C_2H_3)OH$. The latter channel generally dominates the kinetics, however, because it involves much stronger attractive forces between the reactants. The resulting alcohol will undergo fragmentation unless it is collisionally stablized.

Hydrogen abstraction is also possible in the reaction of atomic oxygen with unsaturated compounds, but its occurrence is negligble at room temperature(24). However, at elevated temperatures, it is expected to become increasingly more important. It is possible that it can even compete with the insertion process in the $O(^1D)$ chemistry(9).

The abstraction and elimination pathways lead to the formation of free radical products that will certainly undergo further bimolecular reaction. The unimolecular fragmentation products will also be highly reactive. All of these fragmentation processes will tend to produce statistical product distributions, with the weakest bonds being the ones most frequently broken. The major difference between ultimate abstraction, elimination, addition and insertion products will most likely be in the amount and nature of the oxygen content. Hydrocarbons and water would be formed from abstraction, carbonyl compounds would be formed from elimination and addition, and hydroxyl compounds from insertion.

IV. $O(^3P)$ + BENZENE

The reactions of $O(^3P)$ with benzene and toluene have also been the subject of considerable study(8,25-29). The measured activation energies(8,25,26), 15-20 kJ/mol, are intermediate between the values found for addition to olefins and hydrogen abstraction. For temperatures as high as 950 K(26), no curvature was observed in the Arrhenius plots of the rate constant data and no hydrogen/deuterium isotope effect was seen. Molecular beam experiments(28,29) have clearly demonstrated that elimination products are dominant under single-collision conditions at collision energies between 10.5 and 41.0 kJ/mol. Curiously, however, for the case of $O(^3P)$ + toluene, Lee and coworkers(29) mainly find methyl elimination products (i.e., phenoxy and methyl radicals). It seems unlikely that a localized biradical adduct should form at that site, exclusively. However, the methyl-phenyl bond energy is about 38 kJ/mol less than the H-phenyl bond energy. Perhaps facile 1,2-oxygen shifts take place until the O-atom migrates around the ring to the methyl carbon, permitting cleavage of the weaker methyl-phenyl bond to occur. This 1,2-oxygen shift would involve epoxide-like intermediate structures. As the *ab initio* quantum chemical study of the ethylene-oxygen adduct(14) provided insight into the mechanism of the $O(^3P)$ + ethylene reaction, we have undertaken a similar study for O + benzene(30).

The initial calculations for the $O(^3P,^1D)$ + benzene system involved determination of the equilibrium geometries for the reactant (benzene), biradical adducts, the addition product (epoxide) and insertion product (phenol). SCF gradient calculations were performed for the closed shell benzene, epoxide and phenol molecules, for the triplet and singlet open-shell biradical adducts and for the triplet epoxide intermediate. The geometry of the lowest energy biradical ($^3A'$) is shown in figure 2. It has one radical electron in what is mainly a benzene π orbital ($16a'$) which is localized on the ortho and para carbons. The other unpaired electron ($17a'$) is localized on the O-atom and lies in the O-C-H plane perpendicular to the C-O bond. The O-C-H bond angle is $103°$ with the O and H atoms evenly distributed above and below the benzene ring plane. The carbon atom involved in the adduct bond is nearly tetrahedral and the C-O and C-C bonds are rather elongated. The individual CASSCF orbital densities are plotted in figure 3 for some of the triplet biradical ($^3A'$) valence orbitals. It can be readily seen that the aromaticity is lost and that one of the unpaired biradical electrons occupies a benzene π orbital while the other is localized on the oxygen atom.

The resulting energies from the SCF, CASSCF and CCI calculations are summarized in Table II. It can be seen that significant differences exist between the experimental energy estimates and the results of the large (MR)-CCI calculations. The approximation that only the benzene π electrons and the O-atom 2p electrons have been correlated is more severe for phenol with its O-H bond than for the biradical. Also a larger basis set would have to be used for more accurate calculations. As was observed for O + ethylene(14), the singlet-triplet energy splittings in the biradicals are quite small. This suggests that interconversion would occur fairly rapidly. The SCF calculations for the $^3A'$ and $^3A''$ biradicals and the $^3A''$ epoxide included determination of the harmonic vibrational force fields and normal mode frequencies. Examination of those results indicated that the structures were all true local minima(18), implying the existence of barriers to the interconversion of biradicals to epoxides or phenols. The locations and heights of these barriers have not been determined in the present study. However, the triplet epoxide is considerably higher in energy than the biradical which makes the possibility of 1,2-oxygen shifts seem unlikely.

The similarity between the energetics for O-atom reactions with ethylene and benzene (or toluene) indicate that the kinetics should also be similar. One expects elimination to dominate under single-collision conditions with addition being most important for bulk gas or condensed phase experiments. At higher energies, hydrogen abstraction would also be expected to play an increasingly more important role. The difference in products between $O(^3P)$ and $O(^1D)$ chemistry under multiple collision conditions is not readily apparent, as the primary addition and insertion products would all undergo secondary fragmentation.

V. IMPLICATIONS FOR POLYMER REACTIONS

It is tempting to extrapolate the reaction mechanisms described above to the case of

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O + polymer reactions under thermal and high energy conditions. One expects the initial reaction steps to involve similar abstraction, addition, elimination or insertion processes. However, a polymer can be thought of as the ultimate condensed phase molecule and rapid stabilization and internal conversion should be possible. In general, fragmentation products should be formed based on their thermodynamic stability and the relative weakness of the bonds being broken. For the case of polystyrene, one might expect to observe a loss of hydrogen atoms (due to abstraction) and phenyl groups (due to elimination and fragmentation) from the chain backbone. The resulting alkyl radicals would probably behave similarly to the intermediate formed in the reaction of $O(^3P)$ with polyethylene.

If translationally hot oxygen atoms were present, small energy barriers would not impede reaction and the abstraction process would probably be enhanced compared to addition or elimination. This change in reaction mechanism means that rate constants cannot readily be extrapolated from the thermal to 5 eV O-atom case. Furthermore, the products for $O(^1D)$ reactions would be similar to those for ground state oxygen at higher energies (the reactions are less discriminating) even though they are quite different at lower energies. Also, it is possible that the magnitudes of the rate constants for the $O(^3P)$ and $O(^1D)$ reactions would be similar at high energies if both processes are limited mainly by the collision rate.

Two other critical factors depend on the condensed-phase nature of the polymer films. If the oxygen atoms are accomodated (*i. e., thermalized*) on the solid surface before reacting, the 5 eV translational energy will not be an important factor and the nuances of the thermal reaction mechanisms will be important. Secondly, under the high vacuum conditions encountered in both LEO and molecular beam experiments, volatilization of moderate molecular weight oligomers will occur. If the O + polymer reaction results in a downward shift in the molecular weight distribution of the polymer, enhanced vaporization will take place which will result in a significant contribution to the measured weight loss in vacuum, but not at higher pressures. These concerns, which are beyond the scope of the present theoretical study, need to be addressed if a comprehensive description of atomic oxygen-polymer reactions is to be developed.

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17. GRADSCF is an *ab initio* gradient program system designed and written by A. Komornicki at Polyatomics Research and supported on grants through NASA.

18. A "stationary" point is defined as a molecular geometry for which all the individual components of the gradient of the energy are zero. At such a point, the second derivatives of the energy correspond to the force constant matrix, the eigenvalues of which are related to the squares of the normal mode vibrational frequencies. If the eigenvalues are all positive, the geometry is a local or global minimum. If one of the eigenvalues is negative, the geometry corresponds to a saddle point.

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Table I. Size of the Calculations

Symmetry[a]	CASSCF[b] $N_{config.}$	(MR)-CCI $N^c_{ref.}$	$N_{config.}$
$^1A'$	2688	6	368,771
$^1A''$	2604	12	792,295
$^3A'$	3756	9	1,143,225
$^3A''$	3804	13	2,225,971
$^3A''^d$	3800	8	573,296

[a] Geometries restricted to C_S symmetry (O and two *para* C atoms lie in the symmetry plane).

[b] 9 orbitals (6 a' and 3 a'') and 10 electrons included in the active space (includes O 2p shell and benzene π orbitals).

[c] Number of reference configurations used in the CCI. For each symmetry and multiplicity this includes all CASSCF configurations with coefficients greater than 0.075 for any geometry.

[d] Epoxide calculations (symmetry plane bisects 2 C-C bonds) based on 5 a' and 4 a'' orbitals in the CASSCF active space.

Table II. Computed Energies[a] for $C_6H_6 + O$ (^3P and ^1D)

Symmetry	SCF[b]	CASSCF[c]	(MR)-CCI	EXPT.[d]
Asymptote				
$^3A''$	0	0	0	0
$^1A''$	215.9			188.7
Biradical				
$^3A'$	151.0	41.8	9.6	(-63.)
$^3A''$		54.0	53.6	
$^1A'$	156.9	51.5	22.2	
$^1A''$		59.4	57.7	
Phenol				
$^1A'$ (S_0)	-106.3	-228.4	-280.7	-428.4
$^3A'$ (T_1)	303.3	156.1	100.8	-87.9
$^1A'$ (S_1)				14.2
$^3A''$		274.1	196.2	
$^1A''$		266.1	202.5	
Epoxide				
$^1A'$ (S_0)	138.5			
$^3A''$ (T_1)	306.7	166.1	144.3	

[a] Energies in kJ/mol.
[b] All geometries optimized.
[c] Calculations at SCF-optimized geometries ($^3A'$ for biradicals and $^1A'$ for phenols).
[d] Based on JANAF Tables and ref. 27.

Summary of previous results for C_2H_4

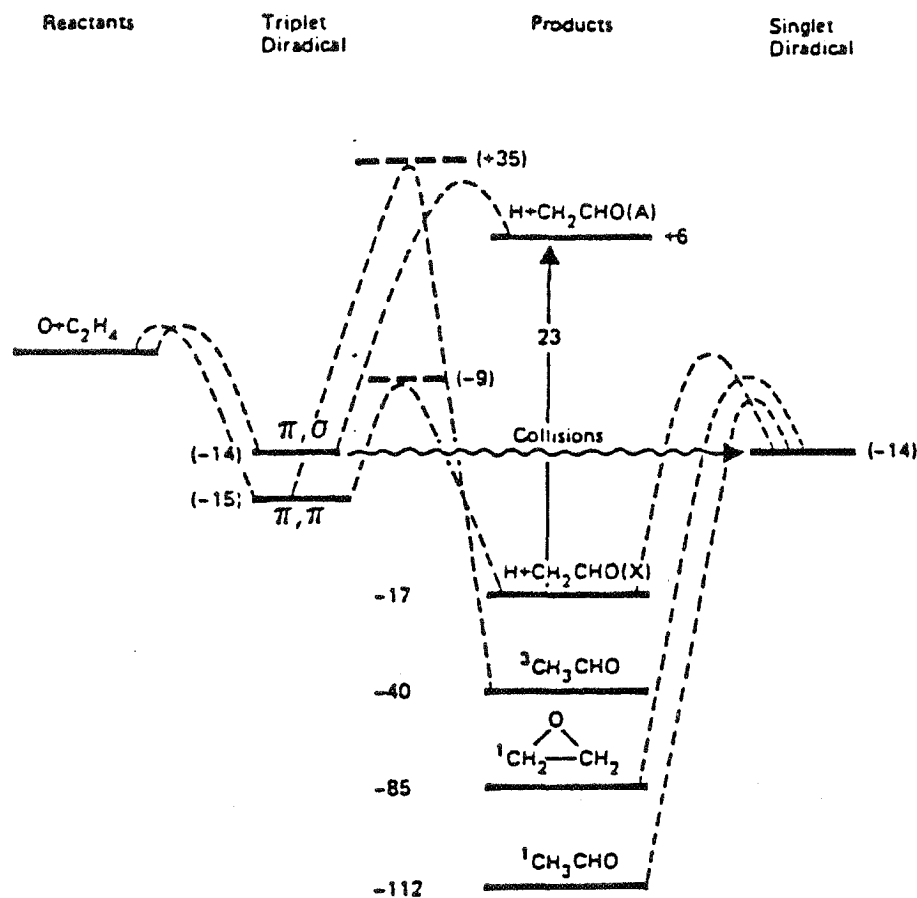- Energy map augmented by calculations of Dupuis *et al.*

Figure 1.

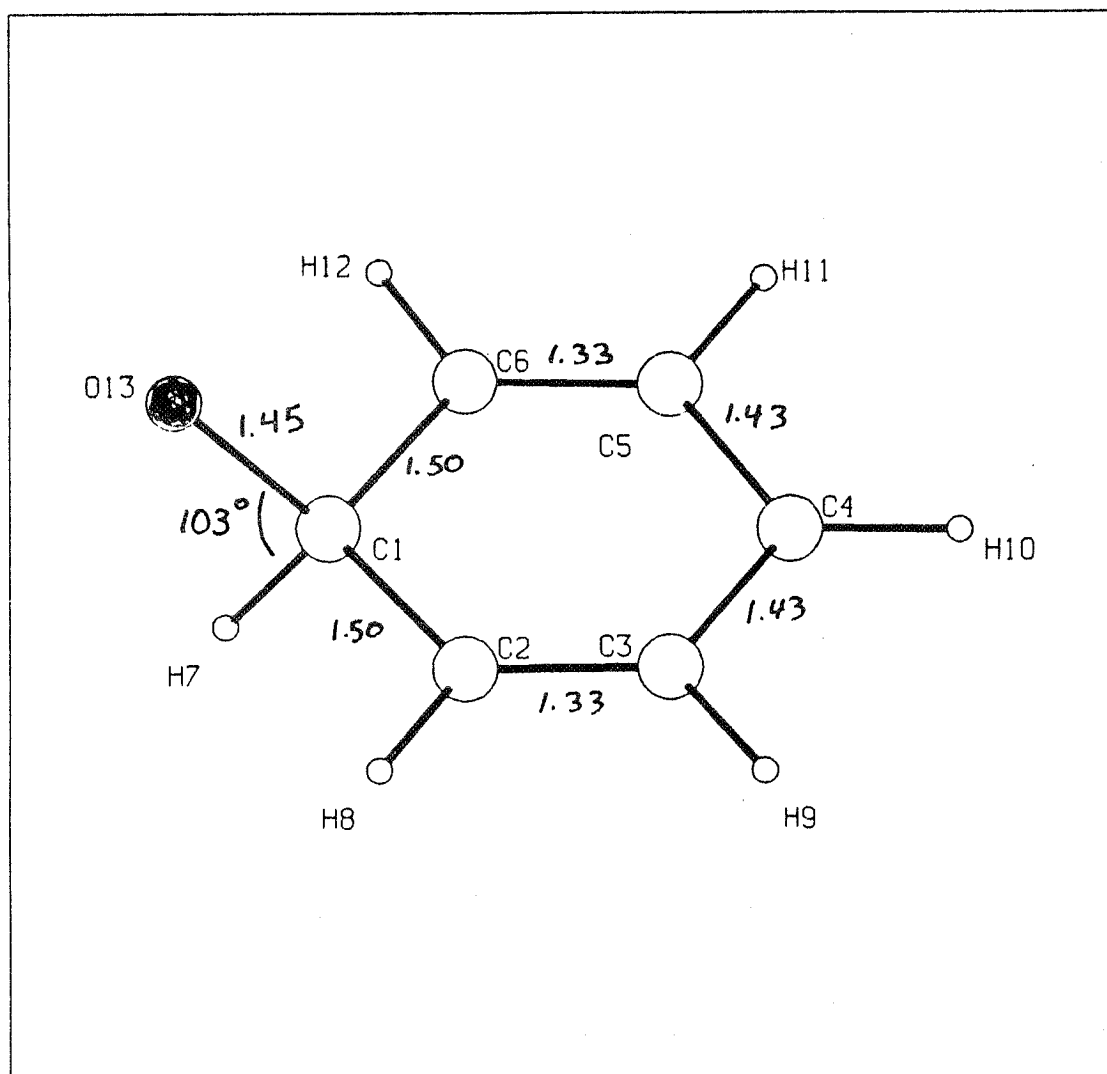# Benzene-O atom biradical geometry

Figure 2.

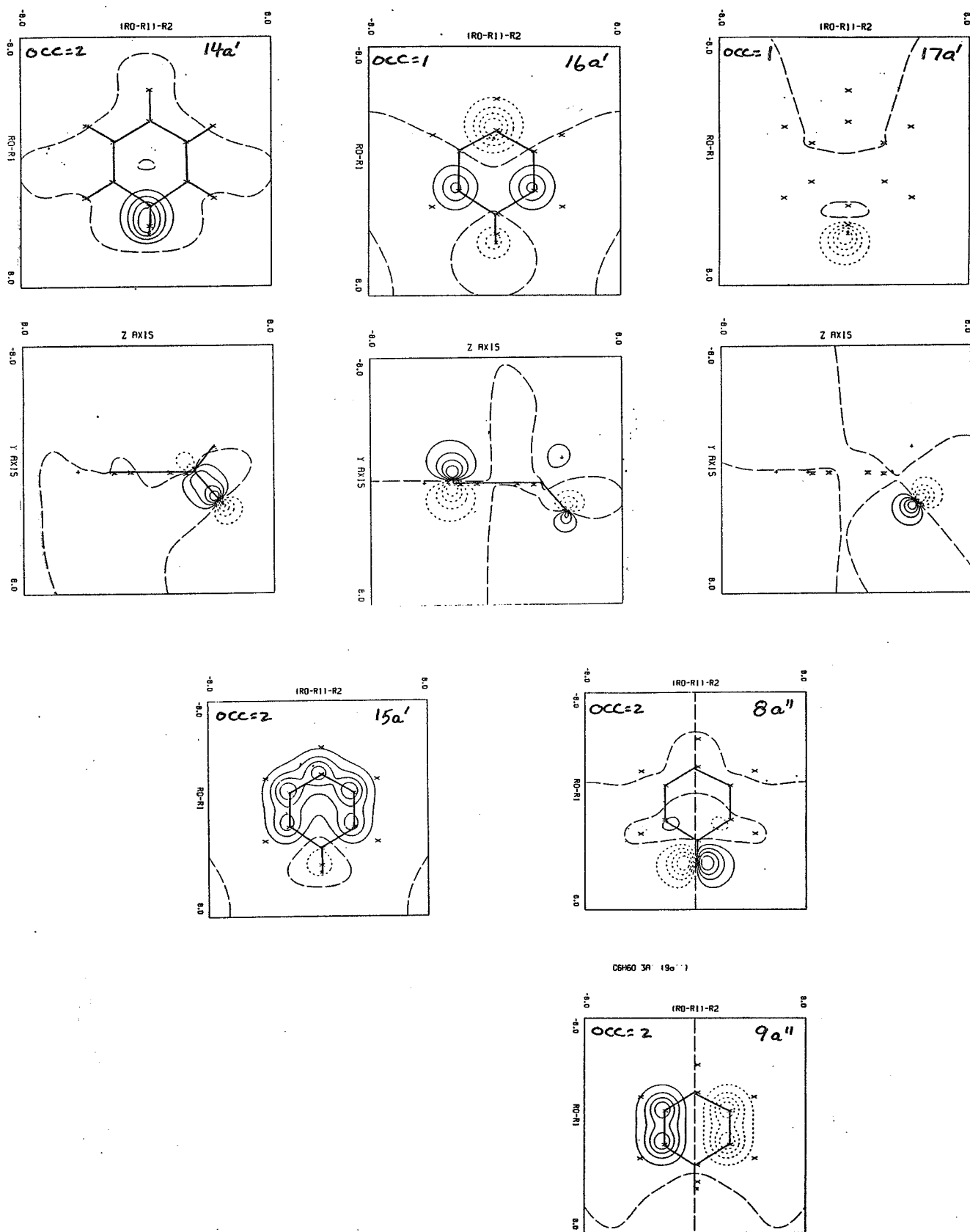# Selected natural orbitals for $^3A'$ benzene-O atom biradical

Figure 3.