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An ab Initio Study of Complexes between Ethylene and Ozone[†]

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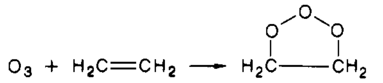
Abstract: A series of complexes between ethylene and ozone have been examined at the SCF, MP2, and MP4(SDTQ) levels of theory within a split-valence-plus-polarization basis. The conformational nature of the primary ozonide (PO) is determined to be an O-envelope, and the theoretically predicted geometry is in excellent agreement with a recently reported microwave structure. The binding energy of PO at correlated levels is computed to be slightly less than 50 kcal/mol, which is also in very good agreement with thermochemical estimates. Five other weakly bound complexes and the transition state to PO have also been investigated.

I. Introduction

The reaction between ethylene and ozone has generated interest across several disciplines. Of immediate environmental impact is the fact that a large part of atmospheric alkene degradation is thought to occur by ozonolysis.[1,2] It has also been determined that the interaction of ethylene with ozone can decrease crop yields and is linked to tree damage.[3]

As the simplest system that can undergo the Criegee mechanism,[4] the C_2H_4/O_3 reaction provides an important point of contact between experimental and theoretical results. The Criegee mechanism was originally proposed for solution-phase ozonolysis;[1,4] however, there is now ample evidence that the same mechanism occurs in the gas phase.[5-9] The first step of the reaction involves the formation of 1,2,3-trioxolane,[10,11] also known as the primary ozonide (PO), by a 1,3-cycloaddition process:



The formation of this intermediate has an experimentally estimated activation barrier of about 5 kcal/mol,[12,13] which is close to an early theoretical estimate.[14] Current interest in the C_2H_4/O_3 system stems from the recently reported gas-phase microwave structure[15] of PO, given in Table I and Figure 1.

Several studies of the SCF conformational surface of PO and substituted PO's have been reported.[16-25] The most comprehensive are those by Cremer,[18-23] who analyzed the surface using puckering coordinates. All possible conformations of a five-membered ring can be described by the pseudorotation angle ϕ with respect to the O-envelope, as defined in Figure 1 with $\phi = 0°$. The surface can be analytically fitted by calculating the energy at the planar geometry, and at values of ϕ equal to 0° (O-envelope) and 90° (twist) which are orthogonal in conformation space. From SCF calculations with a double-ζ-plus-polarization (DZP) basis, a pseudorotation barrier in PO was determined as 3.5 kcal/mol and the barrier to planarity as 7.7 kcal/mol. The lowest energy conformation of PO was found to be the O-envelope.

The results of Cremer[18-23] differ from those of Ruoff et al.,[24,25] who have found a very large difference in the energy of the O-envelope ($\phi = 0°$), the O-adjacent-envelope ($\phi = 36°$), and the C-envelope ($\phi = 72°$). These three structures are reported to be minima at the double-ζ (DZ) SCF level with the O-envelope slightly more stable. The DZ geometries were then used to determine relative energies by a four-configuration MCSCF treatment, in which the O-adjacent-envelope and the C-envelope were predicted to be more stable than the O-envelope by about 40 kcal/mol. These MCSCF results are inconsistent with a recent microwave study,[15] which finds the O-envelope as the only conformation in the gas phase.

Table I. Geometrical Parameters for PO, Ozone, and Ethylene at the SCF and MP2 Levels Using the 6-31G(d,p) Basis (Bond Lengths in Å and Bond Angles in deg)

parameter	SCF	MP2	exptl
	O-Envelope Conformation of PO		
r(OO)	1.382	1.458	1.453[a]
r(CO)	1.407	1.426	1.417
r(CC)	1.541	1.547	1.546
$r(CH_{endo})$	1.083	1.089	1.088
$r(CH_{exo})$	1.081	1.087	1.095
∠OOO	102.7	100.3	100.2
∠OOC	103.3	100.9	102.1
∠OCC	102.7	104.0	103.9
∠HCH	110.1	110.6	111.6
$\angle CCH_{endo}$	111.8	110.9	111.2
$\angle OCH_{exo}$	107.3	106.2	
α	131.1	127.1	129.2
	Ethylene		
r(CC)	1.316	1.334	1.339[b]
r(CH)	1.076	1.080	1.086
∠HCC	121.7	121.6	121.2
	Ozone		
r(OO)	1.204	1.299	1.278[b]
∠OOO	119.0	116.3	116.8

[a] Reference 15. [b] Herzberg, G. *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structures of Polyatomic Molecules*; Van Nostrand: New York, 1966.

Since the limited MCSCF approach includes some electron correlation while the SCF treatment obviously does not, the

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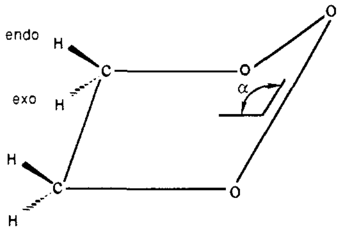
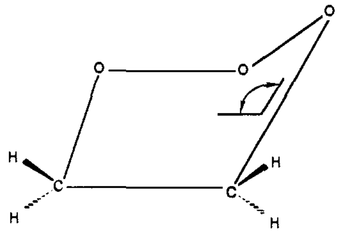
Table II. Relative Energies (kcal/mol) of Various Species at Different Levels of Theory Using the 6-31G(d,p) Basis[a]

	symmetry	SCF	MP2	MP4(SDTQ)[b]	exptl
$O_3 + C_2H_4$	C_{2v}, $D_{\infty h}$	0 (0)	0 (0)	0	0
π-complex (A)	C_s	−0.9 (−0.5)	−6.2 (−5.8)	−0.8 (−0.4)	
σ-complex (B)	C_s	−0.04[c]	−0.6[c]		
out-of-plane (C)	C_{2v}	−0.3[c]	−1.4[c]		
in-plane (D)	C_{2v}	−0.5[c]	−1.7[c]		
trans (E)	C_s	*d*	−0.8[c]		
TS	C_s	14.1 (16.3)	3.3 (5.5)	0.3 (2.5)	5[e]
PO (O-envelope)	C_s	−86.0 (−80.5)	−49.2 (−43.7)	−51.5 (−46.0)	−45 ± 6[f]

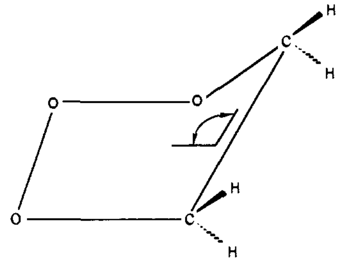
[a] A zero-point correction is added from SCF vibrational frequencies calculated at the SCF geometry and scaled by a factor of 0.9. These values are reported in parentheses. [b] Evaluated at the MP2 geometry. [c] Zero-point correction not calculated. [d] No minimum found. [e] References 12 and 13. [f] Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976. There is also a full CI estimate of −49 kcal/mol in ref 21.



O - envelope



O - adjacent - envelope



C - envelope

Figure 1. Three conformations of the primary ozonide 1,2,3-trioxolane (PO) are shown: the O-envelope, the O-adjacent-envelope, and the C-envelope. The O-envelope is the only experimentally observed conformation (see Table I for calculated and experimental geometries).

disagreement between the results of Cremer and those of Ruoff et al. is unresolved. However, correlation is not expected to be important in determining the preferred conformation of PO since each conformer has the same number and types of bonds. Rather, the discrepancy between these theoretical studies is probably due to the basis set used by Ruoff et al., which lacked polarization functions. In addition, their geometries were determined only at the SCF level by a pointwise search rather than with gradient techniques followed by analytic second derivatives for confirmation of true minima.

II. Computational Methods

Full geometry optimizations were performed at the SCF and MP2 levels by gradient techniques with the GAUSSIAN 86 series of programs[26] using the 6-31G(d,p) basis set.[27,28] At the SCF level, harmonic vibrational frequenices and zero-point vibrational corrections were computed by analytic second-derivative techniques. Since it is not feasible to perform complete geometry optimizations at the MP4(SDTQ) level for all the structures considered here, MP2 geometries are assumed for the single-point MP4(SDTQ) calculations. This is justified by the fact that MP2 predicts accurate geometries for the species of interest here (see Table I for comparison to experiment for O_3, C_2H_4, and PO). MP relative energies are more uncertain since the perturbative treatment of electron correlation requires a dominant configuration that is certainly not the case for ozone.

III. Primary Ozonide

The SCF and MP2 equilibrium geometries for the O-envelope conformation of PO are compared with the experimental microwave structure in Table I. The O–O bond lengths are greatly underestimated at the SCF level, as expected.[29] However, the MP2 geometry is in excellent accord with experiment. The equilibrium structures of O_3 and C_2H_4 are also compared with experiment in Table I. Optimizations at the SCF and MP2 levels which were begun at assumed starting geometries for the O-adjacent-envelope and C-envelope collapsed without activation to the O-envelope.

Thus, the O-adjacent-envelope and C-envelope conformations reported by Ruoff et al. do not exist at the levels employed in the present study. As discussed earlier, their results are in part due to the lack of polarization functions in their basis set. Cremer has concluded that such functions are essential in calculating accurate conformational barriers in PO.[18]

The gas-phase dipole moment[15] of PO was measured to be 3.43 D. The SCF dipole moments for the O-envelope at the SCF and MP2 geometries are calculated to be 3.90 and 4.03 D, respectively.

IV. Other Complexes between Ozone and Ethylene

The rotational constants and dipole moment for a weakly bound complex of ozone and ethylene are currently under investigation experimentally.[30] In the present work, five candidate structures for this complex have been obtained at the MP2 level and four at the SCF level. The geometries, which are depicted in Figure 2, can be labeled as a π-complex (A), a σ-complex (B), and three hydrogen-bonded complexes (C–E). The energetics of each is given in Table II. The π-complex is 6.2 kcal/mol more stable than O_3 and C_2H_4 at the MP2 level, but this is lowered to 5.8 when SCF zero-point corrections are included. Basis set superposition effects at the MP2 level[31] are unlikely to affect the predicted existence of the π-complex since it is the most bound of the species A–E.

The π-complex, which has been suggested by matrix spectroscopy of ozone with certain alkenes,[32] is stabilized by the mutual

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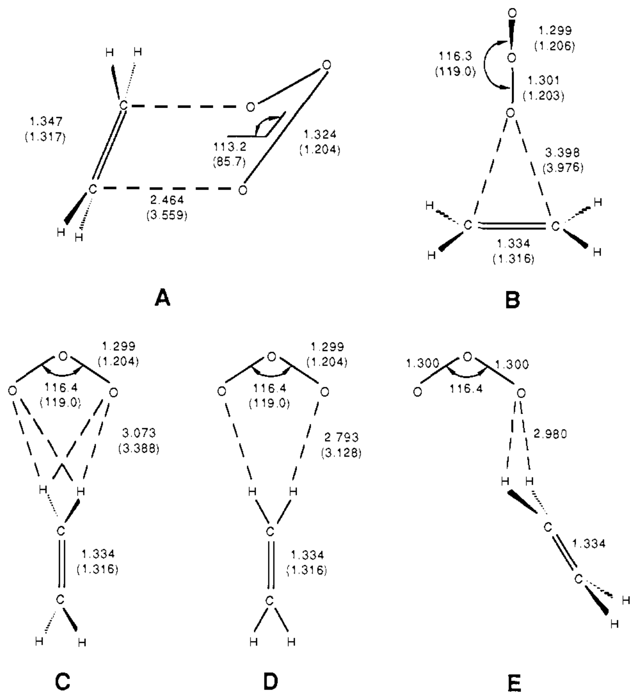

Figure 2. Predicted complexes between ozone and ethylene. Structures A and B are π- and σ-complexes, respectively, while C–E are hydrogen-bonded complexes. Selected geometrical parameters are listed for the MP2 level and the SCF level (in parentheses). A minimum was not found for E at the SCF level.

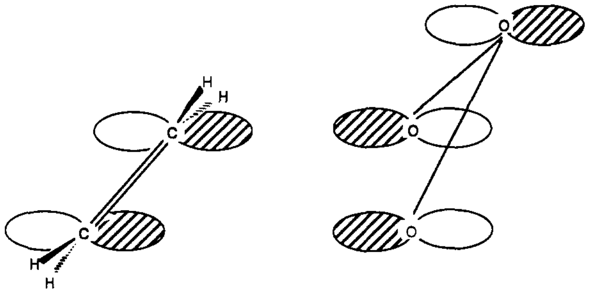

Figure 3. A schematic orbital depiction of the important stabilizing interaction in the π-complex. The π orbital of ethylene (HOMO) can overlap with the π^* orbital of ozone (LUMO).

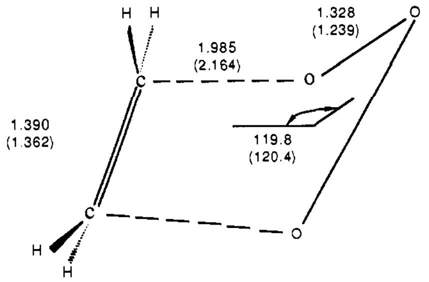

Figure 4. Transition state for formation of PO from the π-complex (A). Selected geometrical parameters are given at the MP2 level and at the SCF level (in parentheses).

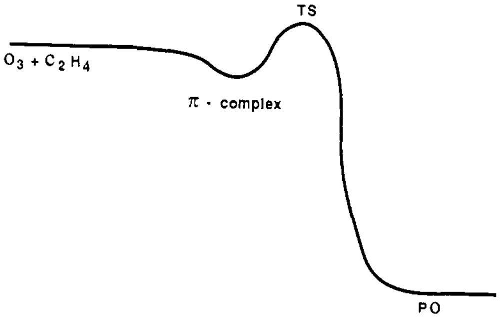

Figure 5. A schematic representation of the formation of PO from ozone plus ethylene.

interaction of the HOMO and LUMO π-like orbitals on each fragment (see Figure 3). At the MP2 geometry, an SCF Mulliken analysis reveals that 0.11e$^-$ has been transferred from ethylene to ozone. A recent gas-phase experiment[30] suggests that the geometry of the complex contains parallel molecular planes of ozone and ethylene, in agreement with the predicted HOMO–LUMO interaction. At the SCF level, the π-complex is much looser (r(CO) = 3.559 Å) and weaker (0.9 kcal/mol) than found at the MP2 level (2.464 Å and 6.2 kcal/mol, respectively). Assuming MP2 geometries, the calculated stability of the π-complex at the MP4(SDTQ) level is lowered to 0.8 kcal/mol (0.4 kcal/mol with SCF zero-point corrections).

V. Transition State of PO

The barrier for addition of an alkene to ozone has been reported as 5 kcal/mol.[12,13] The addition of ethylene is found to occur concertedly at the SCF level as evidenced by the presence of one negative eigenvalue in the force constant matrix. The nature of the stationary point was not further characterized at the MP2 level. However, a recent study of the addition of nitrone (isoelectronic with ozone) to ethylene found the concerted transition state 14.7 kcal/mol lower in energy than the non-concerted transition state at the MCSCF+CI/4-31G level.[33] Thus it is likely that the C_2H_4/O_3 reaction also occurs concertedly at correlated levels.

Yamaguchi et al.[34] have recently reported a barrier of 10.0 kcal/mol for the cyclic transition state in the addition of ozone to ethylene relative to reactants from APUMP2/6-31G* calculations (approximate projected MP2) on 4-31G optimized geometries, but the authors conclude that the true activation energy is less. The transition state calculated here (Figure 4 and Table II) is 3.3 kcal/mol above ethylene and ozone at the MP2 level. With respect to the π-complex, the barrier becomes 9.5 kcal/mol, which is increased to 11.3 kcal/mol when SCF zero-point corrections are included. MP4(SDTQ) single-point calculations at the MP2 geometries change these values to 1.1 and 2.9 kcal/mol, respectively. The MP2 distance between ethylene and ozone decreases by 0.479 Å and the flap angle increases by 6.6° on proceeding from the π-complex to the transition state. The largest electronic effect is the increasing interaction of the π orbital of ethylene with the antibonding orbital of ozone (Figure 3).

VI. Conclusions

A schematic representation of the reaction between ozone and ethylene to form PO is given in Figure 5. Table II summarizes the calculated energetics of complex formation at the SCF, MP2, and MP4(SDTQ) levels with 6-31G(d,p) basis set. Using SCF DZP geometries, Cremer has determined the energy of PO relative to ozone plus ethylene to be −77.6 and −49.2 kcal/mol at the SCF and MP2 levels, respectively,[21] in reasonable agreement with the present values. The MP2 geometry of PO computed here is in excellent accord with a recent microwave structure,[15] and its relative energy with respect to ozone and ethylene is in the range provided by thermochemical estimates.

Also, ozone and ethylene are predicted to form a π-complex, which is bound by 6.2 kcal/mol at the MP2 level. At the MP2 geometries, MP4(SDTQ) single-point calculations reduce this stability to less than 1 kcal/mol. However, the π-complex would undoubtedly become more stable if its geometry were optimized at the MP4(SDTQ) level and be bound by at least 1 or 2 kcal/mol.

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Note Added in Proof. The microwave structure of the C_2H_4/SO_2 complex has recently been determined.[35] It has a structure similar to the C_2H_4/O_3 complex,[30] where the two molecular planes are roughly parallel indicating an interaction between the π systems.

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Registry No. PO, 6669-36-9; ethylene, 74-85-1.

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Electronic Structure and Spectra of Uranocene

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Abstract: The wave functions and energy levels for uranocene, $U(C_8H_8)_2$, have been computed using ab initio techniques including the spin–orbit interaction and relativistic core potentials. The results give detailed information on the bonding in the ground state and on the assignment of the visible spectrum. A large amount of mixing of the ligand π orbitals with the uranium 6d (and 5f) orbitals was found, confirming expectations of sizable covalent bonding. The symmetry of the ground state was found to be E_{3g}, in agreement with some previous experimental and theoretical results. There are many low-lying $5f^2$ excited states, only two of which have been observed, as well as 5f → 6d, $\pi \rightarrow$ 6d, and $\pi \rightarrow$ 5f excited states. The visible bands, which give uranocene its green color, previously thought to be ligand-to-metal bands, are found to be primarily due to 5f → 6d excitations. The basis set of 208 generally contracted Gaussian symmetry orbitals is of slightly better than double-ζ quality, and 32 carbon core electrons and 78 uranium core electrons were replaced by relativistic core potentials. Double-group symmetry-adapted configuration-interaction expansions up to 31 000 in length were used. Spin–orbit matrix elements were included in the Hamiltonian matrices.

Background. Uranocene, $U(C_8H_8)_2$, was first prepared by Streitwieser and Müller-Westerhoff[1] in 1968. One of their reasons for making this compound was that the uranium 5f orbitals might play a significant role in the metal–ligand bonding, analogous to the role of the iron 3d orbitals in ferrocene.

Uranocene is quite a stable compound and, as shown by X-ray crystallography,[2] has the anticipated "sandwich" structure. Its reactivity properties have been studied extensively[3-5] and many substituted uranocenes and other actinocenes have been synthesized.[4-8]

Uranocene's most distinctive physical properties are its paramagnetism and its green color.[1] Thus, its magnetic and spectroscopic properties have been studied extensively and, together with simple theoretical calculations, have yielded some information on its electronic states although this information is far from complete. In particular, the ground state of uranocene has not been conclusively assigned and the electronic spectra remain unassigned.

Theoretical Method. The accurate calculation of the electronic structure of molecules containing heavy atoms requires being able to deal not only with large numbers of electrons and the subtleties of electron correlation but also with the large magnitude of the spin–orbit effect and other relativistic effects. It has been shown that relativistically derived core potentials and spin–orbit operators provide a means by which all these difficulties can be addressed effectively.[9-13]

In this work the wave functions and energy levels for uranocene have been computed using these ab initio techniques. The many-electron wave functions were expanded in double-group symmetry-adapted functions. These configuration–interaction (CI) expansions are of modest length, but spin–orbit matrix elements were included in the corresponding Hamiltonian matrices.

Questions Studied. The theoretical results give information on several questions of basic interest to the electronic structure of uranocene. In particular, these include (1) the role of uranium orbitals in covalent bonding to the ligands, (2) the identification of the ground state, whether the weak field or strong field case applies and whether LS coupling or jj coupling applies, and (3) the assignment of the visible spectrum in terms of the nature of the excited states.

Previous Work

Preparation and Chemical Properties. In 1968, Streitwieser and Müller-Westerhoff[1] used potassium to generate $C_8H_8^{2-}$ ions in tetrahydrofuran solution and then added UCl_4 to prepare uranocene.

$$4K + 2C_8H_8 + UCl_4 \xrightarrow{THF} U(C_8H_8)_2 + 4KCl$$

Uranocene, when crystallized, is green, sublimes at 180 °C, and

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