

Electronic Structure of Unstable Intermediates

III. The Electronic Structure of OCC

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The geometry of the species OCC has been investigated within the restricted Hartree-Fock LCAO–MO–SCF approximation. Several one electron properties have been calculated at the calculated minimum energy configuration of $R(O-C) = 2.121$ bohr, $R(C-C) = 2.58$ bohr.

Key words: Unstable intermediates – Calculated geometry

Introduction

This paper reports *ab initio* calculations on the triplet, OCC, and represents another in the series of papers from this Department, dealing with the electronic structure of unstable intermediates. The species has been observed by IR spectroscopy in an argon matrix by Milligan and Jacox [1]. They observed this species 1) on photolysis of matrix-isolated cyanogen azide in the presence of carbon monoxide (at a wavelength less than 2800 Å) and 2) by vacuum UV photolysis of matrix-isolated carbon suboxide. Features of the IR spectra obtained from these systems were interpreted by Milligan and Jacox as arising from a linear species, OCC.

Our theoretical examination of the system was prompted by their observations, together with the existence of a corpus of work postulating the presence of OCC as an intermediate in a variety of chemical processes, including: radiolysis of carbon dioxide [2]; photolysis of carbon suboxide [3]; thermal decomposition of carbon suboxide [4]; UV photolysis of carbon monoxide [5]; and, pulse radiolysis of carbon monoxide [6].

In the work by Bayes [3], there is reported results of a semi-empirical calculation on OCC, with bond lengths taken from those experimentally determined for carbon suboxide ($R(C-O) = 2.1921$ bohr; $R(C-C) = 2.4170$ bohr). These bond lengths were also used by Olsen and Burnelle [7] in another semi-empirical calculation. It is suggested by Bayes that the ground state of OCC is $^3\Sigma^-$, with low-lying $^1\Sigma^+$ and $^1\Delta$ excited states. Baker et al. [8] showed that their results of photolysis of carbon suboxide in presence of alkenes are consistent with the existence of the two multiplicities (triplet at lower, singlet at higher energies of photolysing radiation).

With the only previous theoretical investigations of this species being semi-empirical, and without geometry optimisation, we have carried out calculations,

determining an optimum equilibrium geometry for the ground state, using *ab initio* LCAO–MO–SCF wavefunctions of similar quality to those used in previous work in this series [9, 10].

Method of Calculation

Calculations were performed on an IBM 360/195, using the programme AL-CHEMY [9]. This programme computes wavefunctions in the Restricted Hartree-Fock approximation, as formulated for open-shell species by Roothaan [11], for linear molecules, over a basis set of Slater-Type Orbitals (STO's). Included in the programme package are routines for the usual Mulliken population analysis [12], and for computing the expectation values of various one-electron operators. In performing the calculations, the total energy was minimised with respect to each bond length, as described in a previous paper [9].

Basis Sets

Three basis sets were used in the calculations, at successively greater levels of quality. The initial calculations were carried out with a double-zeta basis set, with exponents taken from the tables of Clementi [13]. This basis set was used to obtain a good first approximation to the bond lengths, after which a further set of calculations were performed using this basis set, augmented by polarization functions of $3d\sigma$, $3d\pi$, $4f\sigma$, $4f\pi$ symmetry on each atom. This basis we refer to as a ($DZ + P$) basis. The polarization function exponents were taken from calculations on CO_2 with a similar basis set by McLean and Yoshimine [14]. The third basis set was the Bagus-Gilbert "best-atom" set – given by McLean and Yoshimine [14], with the polarization functions taken from their calculation on OCN^- . Energy results are reported in hartrees, distances in bohrs.

Results

The geometries investigated, together with the total energies and the virial coefficients are given in Table 1, for each basis in turn.

Calculations with the double zeta basis gave an optimum geometry of: $R(\text{O}-\text{C}) = 2.205$ bohr; $R(\text{C}-\text{C}) = 2.645$ bohr.

For the set of calculations using the $BA + P$ basis set, the optimum geometry was taken as $R(\text{O}-\text{C}) = 2.121$ bohr; $R(\text{C}-\text{C}) = 2.58$ bohr (from total energy vs. bond lengths curves). The total energy was calculated at this geometry, together with expectation values of various one-electron operators. These expectation values are listed in Table 2. At this geometry also, SCF calculations were performed on the anion and cation of the species. Comparison of the orbital and total energies, together with the calculated vertical ionisation potentials are given in Table 3. Summaries of part of the Mulliken population analyses for the three species, OCC , OCC^+ , OCC^- , are given as Table 4. Values, derived from the expectation values, for observable properties, are given in Table 5.

Table 1. Energy results

Bond O-C	Lengths C-C	Total energy	Virial
Calculations with the (<i>DZ</i>) basis			
2.2	2.63	-150.36982	-2.00027
2.2	2.65	-150.36985	-2.00040
2.2	2.60	-150.36955	-2.00007
2.2	2.67	-150.36976	-2.00051
2.15	2.65	-150.36812	-1.99953
2.25	2.65	-150.36893	-2.00116
2.22	2.65	-150.36977	-2.00071
2.205	2.645	-150.36987	-2.00045
Calculations with the (<i>DZ + P</i>) basis			
2.2	2.64	-150.50279	-2.00205
2.1	2.64	-150.50579	-2.00016
2.1	2.65	-150.50555	-2.00023
2.1	2.645	-150.50568	-2.00019
Calculations with the <i>BA + P</i> basis			
2.10	2.645	-150.51518	-2.00007
2.11	2.645	-150.51538	-2.00028
2.12	2.645	-150.51544	-2.00048
2.14	2.645	-150.51518	-2.00088
2.126	2.645	-150.51541	-2.00060
2.122	2.645	-150.51543	-2.00052
2.122	2.65	-150.51531	-2.00056
2.122	2.55	-150.51615	-1.99975
2.122	2.5	-150.51489	-1.99926
2.122	2.4	-150.50778	-1.99808
2.122	2.3	-150.49262	-1.99601
2.121	2.58	-150.51632	-2.00000

Table 2. Expectation values of quoted operators for OCC

Operator	Value at centre:		
	O	C	C
$1/r$	26.3283	20.6671	18.7191
z	41.4454	- 0.974598	- 52.5746
z^2	178.9141	93.0755	231.2325
r^2	202.6915	116.8530	255.0099
ϱ^2	23.7774	23.7774	23.7774
z/r^3	1.61589	- 0.87573	- 1.26289
$(3z^2 - r^2)/r^5$	0.72398	1.58626	0.06949

Table 3. Orbital energies for OCC and ions

Orbital	OCC ⁺	OCC	OCC ⁻
1σ	-21.038	-20.6862	-20.3641
2σ	-11.7536	-11.4207	-11.0932
3σ	-11.7085	-11.3051	-10.9763
4σ	- 1.8704	- 1.5541	- 1.2534
5σ	- 1.3935	- 1.0335	- 0.7072
6σ	- 1.1109	- 0.8005	- 0.5076
7σ	- 0.8283	- 0.4891	- 0.1894
1π	- 0.9849	- 0.6848	- 0.3996
2π	- 0.7809	- 0.4689	- 0.0847

Total energy comparison		
Species	Total energy	Virial coefficient
OCC	-150.5163	-2.0000
OCC ⁺	-150.1187	-1.9996
OCC ⁻	-150.5347	-1.9991

Vertical ionisation potentials	
OCC→OCC ⁺	0.3976 a.u.
OCC→OCC ⁻	- 0.0183 a.u.

Table 4. Mulliken population analysis-summary of results for OCC, OCC⁺, OCC⁻:

	O	C	C
OCC: Total atomic populations for valence orbitals			
4σ ²	1.45823	0.53109	0.01069
5σ ²	0.06720	1.10483	0.82797
6σ ²	1.72910	0.21069	0.06021
7σ ²	0.01567	0.15373	1.83060
1π ⁴	2.69098	1.12975	0.17927
2π ²	0.17680	0.53506	1.28814
Total	8.13800	5.66614	6.19586
OCC ⁺ : Total atomic populations for valence orbitals			
4σ ²	1.47100	0.51922	0.00978
5σ ²	0.03913	1.09146	0.86941
6σ ²	1.77000	0.19294	0.03706
7σ ²	0.01652	0.12449	1.85899
1π ⁴	2.49197	1.28644	0.22159
2π ¹	0.09415	0.20444	0.70141
Total	7.88256	5.42034	5.69710
OCC ⁻ : Total atomic populations for valence orbitals			
4σ ²	1.44895	0.53771	0.01334
5σ ²	0.10239	1.09373	0.80388
6σ ²	1.67790	0.22596	0.09614
7σ ²	0.01549	0.18303	1.80148
1π ²	2.83845	0.99191	0.16964
2π ³	0.28068	0.95468	1.76464
Total	8.36403	5.98781	6.64816

Table 5. Molecular properties calculated from expectation values

Property		Value (a. u.)	(CGS)
Dipole moment		-0.5314	- 1.305 <i>D</i>
Quadrupole moment		-4.3415	-5.8469 barn
Field gradients	O	2.5575	
	C	0.7914	
	C	0.7833	
<i>g</i> values	<i>g_s</i>	0.5041	
	<i>g_r</i>	0.1292	
Force on nuclei	O	0.0855	
	C	0.0071	
	C	0.0005	
Force constants:	Bond O-C	1.2916	2.0108 × 10 ⁶ dyn cm ⁻¹
	Bond C-C	0.61076	9.5083 × 10 ⁵ dyn cm ⁻¹

Discussion

All calculations refer to the ground state configuration:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^2, {}^3\Sigma^-,$$

as reported by Milligan [1].

The minimum energy of -150.51632 hartree obtained from the *BA + P* investigation corresponds to bond lengths of $R(\text{O}-\text{C}) = 2.121$ bohr and $R(\text{C}-\text{C}) = 2.58$ bohr. This suggests a stronger O-C bond than in C_3O_2 (where the bond length is 2.192 bohr) and a weakened C-C bond (2.58 bohr as against 2.417 bohr in C_3O_2). The optimum geometry as calculated with the *BA + P* basis correlates with that obtained in an *ab initio* calculation on C_3O_2 by Sabin and Kim [15], using a (7*s*, 3*p*) Gaussian basis set, contracted to <5, 2>; that is, a basis set without polarisation functions. They obtained optimum bond lengths of 2.349 bohr for the carbon to oxygen distance and 2.517 bohr for the intercarbon distance. Our calculations show, in comparison, a reduced carbon-oxygen bond length and a lengthened carbon-carbon bond. This can be interpreted as indicating that the triatomic system is approaching one of a carbon monoxide molecule plus a perturbing centre.

We turn now to consideration of the total energy of the system. As a generalisation, the computed total molecular energy for a given basis will be at least as far from the true Hartree-Fock value, as the sum of the separated atom energies - for the same basis - is from the sum of the separated atom Hartree-Fock energies. The total energy will deviate further with decreasing flexibility of basis set [16].

The deviation from Hartree-Fock of the atomic energies with the *BA + P* basis set is about 0.0002 hartree, and we can conclude that the energy as computed

is within 0.005 hartree of the Hartree-Fock limit [9]. The difference between this and the sum of the atom energies gives the contribution to the dissociation energy from a wavefunction with this basis. With the Best-Atom basis set, the atomic energy of oxygen (3P state) is -74.80938 hartree, that of carbon (3P state) is -37.68802 hartree; thus, the sum of the atomic energies is -150.18542 hartree. The difference between this and the total molecular energy, -150.51632 , is 0.33000 hartree (the Hartree-Fock contribution to the dissociation energy would be expected to be about 0.005 hartree larger) [9].

The full population analysis, which we have reported summarily in Table 4, indicates that contribution to the bonding description by the polarisation function becomes significant for only the highest-energy orbitals; that is, the π -set and the two highest σ -orbitals. It can be concluded that this basis is relatively complete; and, that the added d and f functions are indeed acting only as polarization functions. A Mulliken population analysis of the orbitals yields a fairly simple description of the bonding orbitals as calculated at the optimum geometry. With the first three σ orbitals corresponding to inner-core, $1s^2$, orbitals on the oxygen and the two carbon atoms, consideration of the usual bonding concepts must focus on the other four σ orbitals, and the two π orbitals.

The 4σ orbital can be considered as corresponding to an oxygen to carbon σ bond of predominantly s character on oxygen, sp on carbon. Similarly, the 5σ orbital can be described as a carbon to carbon σ bond, predominantly sp on the central, s on the terminal carbon atom. The two highest orbitals, 6σ and 7σ , correspond to sp lone pair orbitals on the oxygen atom and the terminal carbon atom. The 1π molecular orbital corresponds to a π -bond, predominantly between oxygen and the central carbon, with a density bias towards oxygen. The 2π orbital corresponds to a π -bond between the carbons, with a less marked density bias, to the terminal carbon.

Population analyses for the single anion and single cation were carried out after the SCF results, from which the effect on the population of removing, or adding an electron from the second π -orbital can be obtained. For the cation, the σ orbitals are practically unaltered, the loss of electron population in 2π being accompanied by a drift of charge towards the terminal carbon, which also occurs to a lesser extent in 1π . The net effect is to localise the positive charge on the central carbon atom. In the anion, the σ orbitals are again almost unperturbed, the extra electron in 2π accommodated by accumulation of electron population on the terminal carbon atom, and further polarization of 1π . The net charge accumulation here is on the terminal carbon atom.

Several properties of the uncharged species, describable in terms of expectation values of one-electron operators, have been calculated. (The formulae for these have been published by McLean and Yoshimine [17, 18].)

We include in Table 5 values for force constants for bond vibrations as indicated. The method used for determining these is similar to that of Pincelli and Cadioli [19]. The difference in total energy from the optimum for each calculation is obtained, together with the difference in bond length from optimum. A least-squares fit of the energy difference as a function of the square of the bond length difference was performed. The coefficient of the quadratic term gives a value for the force constant.

Conclusion

The geometry of the species OCC has been investigated within the restricted Hartree-Fock LCAO-MO-SCF approximation. Several properties, describable in terms of one-electron operators have been calculated at the computed minimum energy geometry of $R(O-C) = 2.121$ bohr, $R(C-C) = 2.58$ bohr.

Of the properties calculated in this work, only the force constants can be compared with experiment. The values quoted by Milligan and Jacox [1] are: for CO bond vibration, 14.06 mdyn \AA^{-1} ; for CC bond vibration, 7.97 mdyn \AA^{-1} . Our calculated values of: 20.0108 mdyn \AA^{-1} for CO bond vibration; and, 9.5083 mdyn \AA^{-1} for CC bond vibration are in tolerable agreement with these values.

We hope that these calculations will stimulate further experimental work on this species.

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