CROATICA CHEMICA ACTA CCACAA **60** (2) 201—206 (1987)

YU ISSN 0011-1643
*CCA-1717* UDC 548.736.372
*Original Scientific Paper*

# Structures and Bonding of Aluminum Dioxygen

*S. P. So*

*Chemistry Department, The Chinese University of Hong Kong Shatin, N. T., Hong Kong*

Received December 13, 1985

Ab initio molecular orbital calculations on the structures of aluminum dioxygen have been performed using double-zeta plus polarization basis functions. The asymmetric bent A1OO isomer is found to be more stable than the symmetric bent OA1O isomer. The A1—O bond is predicted to be best described as covalent with a substantial ionic character.

## INTRODUCTION

Extensive studies on the preparation and characterization of the oxides formed from alkali and alkaline-earth metal atoms and oxygen molecules in inert matrices have been carried out by Andrews and coworkers over the past fifteen years.[1–12] The superoxides $MO_2$ were formed for all alkali metals M. The IR and Raman spectra which were used to establish their formation could be interpreted on the basis of the ionic model $M^+O_2^-$.[5] However, spectroscopic data provided no direct information on the electron-density distribution in a molecule, and thus the authors felt that it seemed reasonable to accept only a cyclic model without any conclusion on the degree of charge transfer. Alkaline-earth metals were found to react to give oxides of the same $MO_2$ formula, whose structure was believed to be the same as that of the alkali metal oxides.[10,11]

Similar works have been extended to Group IIIA metals.[13–15] Their oxides are also of the $MO_2$ form. By analogy with the alkali and alkaline-earth metal dioxygen $MO_2$. Serebrennikov *et al.*[15] assumed a cyclic ionic structure of $C_{2v}$ symmetry for these Group IIIA metal oxides.

Recently, Sonchlk et al.[16] demonstrated that the principal reaction product in $N_2$ matrices of Al with either $O_2$ or $O_3$ was an asymmetric and highly bent A1OO molecule ——— very little of this species was produced in Ar matrices. The cyclic $C_{2v}$ structure for this aluminium dioxygen molecule was ruled out by the consideration of its G-matrix elements and the oxygen-isotopic shifts.

Should the asymmetric bent structure suggested by Sonchlk *et al.*[16] be the true one for $AlO_2$, it would be most interesting because it would then represent the first example of a bent metal dioxygen molecule which is not of $C_{2v}$ symmetry.

The bent structure, which molecules such as HOO[17], FOO[18], and ClOO[19] are known to have, implies that the bonding in AlOO is predominantly covalent.[16] The present work was thus performed with the hope of determining the hitherto unknown geometry of aluminium dioxygen and gaining some insight into its bonding.

## CALCULATIONS

The potential energies of $AlO_2$ under $C_{2v}$ and $C_s$ symmetries were calculated using the Cal Tech-Ohio State-Berkeley CDC version of POLYATOM implemented on our IBM3031 computer.[20] This package of programmes has the provision of calculating various states by specifying their electronic configurations in the input. The basis sets used for Al and O are the ones contracted from primitive gaussian functions generated by Huzinaga to double-zet sets (DZ) by Dunning.[21,22] The primitive sets are (11s 7p) for Al and (9s 5p) for O, and are contracted to [6s 4p] and [4s 2p], respectively. These double-zeta sets are then augmented by six 3d functions (DZ+P) of exponent 0.6 for Al and 0.85 for O. The importance of 3d polarization functions in the prediction of geometries of some molecules containing the second-row central atoms has been well demontrated.[23] Though Al is not the central atom in the asymmetric AlOO molecule, d-functions have been found essential in this case to predict the molecular geometry correctly (see below).

## RESULTS AND DISCUSSION

Initially, trial calculations were made using the DZ basis functions on the asymmetric AlOO molecule under $C_s$ symmetry. However, optimization of the bond angle extrapolated to a linear geometry, which is in contradiction to the IR result.[16] Subsequent computations were therefore performed using the DZ+P basis functions. The species was found to have an asymmetric bent structure in its ground state which is of $^2A''$ symmetry arising from the electronic configuration $\ldots(12a')^2(3a'')^1$. Its calculated bond angle of 100.9° is in excellent agreement with the value of 100° selected by Sonchlk *et al.*[16] from the consideration of its G-matrix elements in relation to the force constanst and observed vibrational frequencies. The calculated properties of the symmetric bent or cyclic OAlO ($C_{2v}$ symmetry) and the asymmetric bent AlOO ($C_s$ symmetry) are listed in Table I. The $C_{2v}$ structure is seen to lie only 1.94 kcal/mol (0.084 eV) above the $C_s$ one. It is interesting to note that the 19-valence-electron $ClO_2$ species also has two isomers. The symmetric bent OClO is a well-known species, kinetically stable at room temperature, while the asymmetric bent ClOO is highly reactive but thermodynamically more stable by about 3 kcal/mole.[24,27] Up to now only the asymmetric AlOO species has been identified. It thus appears that AlOO is both kinetically and thermodynamically more stable than OAlO.

Triatomic molecules with twelve to sixteen valence electrons are predicted by Walsh's rule[28] to be linear in their ground and low-lying excited electronic states. This prediction is well established experimentally for many molecular species, e. g. $CO_2$, $C_3$, OCS, etc. AlOO has fifteen valence electrons, and yet is predicted here quantum-mechanically to be bent both in its $^2A''$ ground state and $^2A'$ first excited state of electronic configuration $\ldots(12a')^1(3a'')^2$ (Table I). However, this is not a unique case. The 12-valence-electron $SiC_2$ molecule has long been thought to be linear in its ground and excited states,[29] but recently has been shown theoretically[30] and confirmed experimentaly[31] to

TABLE I

*Calculated Molecular Parameters of $AlO_2$*

| Symmetry | State | $R_{AlO}$ (Å) | $R_{OO}$ (Å) | $\Theta$* (deg) | $\mu$ (D) | $E$ (a. u.) |
|---|---|---|---|---|---|---|
| $C_{2v}$ | $^2A_2$ | 1.900 | 1.291 | 39.73 | 1.19 | —391.5676 |
| $C_s$ | $^2A''$ | 1.776 | 1.333 | 100.88 | 1.92 | —391.5707 |
|  | $^2A'$ | 1.718 | 1.320 | 141.76 | 1.63 | —391.5657 |

* $\Theta$ is $<$ OAlO for $C_{2v}$ and $<$ AlOO for $C_s$ structure.

TABLE II

*Mulliken Populations for $AlO_2$*

|  |  | Al | O* | O |
|---|---|---|---|---|
| $^2A_2$ | s | 5.895 | 3.882 | 3.882 |
|  | p | 6.449 | 4.384 | 4.384 |
|  | d | 0.021 | 0.052 | 0.052 |
|  | total | 12.365 | 8.318 | 8.318 |
| $^2A''$ | s | 5.907 | 3.852 | 3.901 |
|  | p | 6.423 | 4.647 | 4.160 |
|  | d | 0.019 | 0.048 | 0.043 |
|  | total | 12.349 | 8.547 | 8.104 |
| $^2A'$ | s | 5.883 | 3.785 | 3.903 |
|  | p | 6.438 | 4.784 | 4.081 |
|  | d | 0.028 | 0.053 | 0.045 |
|  | total | 12.349 | 8.622 | 8.029 |

* Central atom in unsymmetric AlOO.

have a cyclic CSiC ground state structure of $C_{2v}$ symmetry which remains unchanged in its first excited state. This cyclic CSiC isomer lies by about 5 kcal/mol[30] below the asymmetric linear SiCC expected from the simple valence theory, probably because of the reluctance of silicon to form multiple bonds. However, the cyclic $C_3$ is less stable than the linear $C_3$ by about 30 kcal/mol.[32] This may be attributed to ring strain.

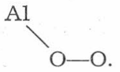
It is important to point out here that, in the case of $SiC_2$, the cyclic isomer is lowered energetically below the linear one only when configuration interaction is included in the calculation.[30] Hence, the present SCF prediction of the bent AlOO being more stable than the cyclic OAlO about 2 kcal/mol should not be taken as absolutely definite. Nevertheless, it seems rather unlikely that correlation energy correction will change this result in view of the fact that the analysis of the electronic spectrum of $SiC_2$ under the assumption of a linear structure had never been completely satisfactory and without controversy before the work of Michalopoulos *et al.*[31] while the matrix IR data of $AlO_2$, on the other hand, pointed strongly to a bent AlOO structure of $C_s$ symmetry.[16] Anyway, a more definite answer cannot be given unless one performs CI calculations with extended basis sets, which, unfortunately, are beyond our limited computing resources. It is thus hoped that this note will stimulate further work along this line.

In the study of the IR spectra of $AlO_2$, $GaO_2$, $InO_2$ and$TlO_2$, Serebrennikov *et al.*[15] assumed a cyclic ionic structure for these species simply in analogy with the ionic model for the superoxides of Group I and Group II metals. However, Sonchlk *et al.*[16] arrived at an asymmetric bent AlOO structure on the basis of normal coordinate consideration. In addition, they suggested that the bent structure, which occurs for molecules such as HOO, FOO and ClOO, implies that the bonding in AlOO is predominantly covalent. $AlCH_3$ has been studied theoretically.[32] Mulliken population analysis yielded $Al^{+0.55}$ $CH_3^{-0.55}$ which implies a considerable measure of ionicity, but the dipole moment was found to be only very small (0.53D). The Al—C bond, was thus considered to be covalent because Fox *et al.* viewed the dipole moment, a nonarbitrary physical observable, as more meaningful in the measure of the character of a bond.

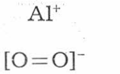
The charge distributions of $AlO_2$ from Mulliken population analysis are given in Table II, and can be represented by $Al^{+0.64}$ $O_2^{-0.64}$ $(C_{2v})$ and $Al^{+0.65}$ $O_2^{-0.65}$ $(C_s)$. These charge seperations arise mainly from the transfer of some Al p-electron density to the anti-bonding $\pi$ orbital of the $O_2$ unit. The dipole moment has been calculated to be 1.92D for the asymmetric AlOO and 1.19D for the cyclic OAlO. These values appear to be somewhat low in view of the large charge separations and the long Al—O bond distances obtained above. However, Mulliken population analysis of the occupied MO's shows that the electronic charge of each of them either mainly localizes at one of the constituent atoms or is almost totally shared by the two oxygen atoms. It is thus concluded that the Al—O bond in $AlO_2$ is best described, in contrast to the suggestion of Sonchlk *et al.*[16], as covalent with a substantial ionic character, unlike $AlCH_3$, HOO, FOO and ClOO. This is in line with the following:

(1) The electronegativity difference between the atoms of the Al—O bond is much larger than those of the Al—C, H—O, F—O and Cl—O bonds. (Electronegativity in Pauling's scale: H=2.1, C=2.5 ,O=3.5, F=4.0, Cl= =3,0, Al=1.5).

(2) The experimental bond lengths of the species $O_2$, $O_2^-$ and $O_2^{-2}$ are 1.208, 1.28 and 1.49Å, respectively. The calculated O—O bond is 1.333Å in the bent AlOO and 1.291Å in the cyclic OAlO. It is thus obvious that in both isomers a considerable amount of electron density has been transferred from the Al atom to the antibonding $\pi$ MO of $O_2$. According to the above conclusion, AlOO can thus be visualized to be formed from an oxygen molecule and a neutral Al atom through the following modes of interaction:



*(I)*



$$\overset{Al^+}{[O=O]^-}$$

*(II)*

*(II)* represents the interaction of a charge-transfer complex, which should have quite a substantial contribution as discussed above. In *(I)*, a metal-oxygen $\sigma$ bond is formed and the unpaired electron is localized at the

terminal oxygen atom. However, this has yet to be proved experimentally by the study of ESR spectrum of AlOO labelled with $^{17}O$.

The force constants of the metal-halogen bonds have been studied for quite a number of molecular species.[33] It has been found that these force constants generally become larger with the increasing ionic character of the bonds. The calculated Al—O and O—O distances of AlOO are 1.776 and 1.333Å, respectively. The observed vibrational frequencies for these bonds are about 1091 and 1337 $cm^{-1}$.[16] The corresponding bond lengths/vibrational frequencies in AlO and $O_2$ are 1.6176Å/978.2 $cm^{-1}$ and 1.2074Å/1580.4 $cm^{-1}$.[34] It is interesting to note that the Al—O vibrational frequency increases with increasing the Al—O bond length. This implies that the Al—O bond of AlOO is more ionic than that of AlO probably due to the readiness of the partly filled antibonding $\pi$ orbital of the $O_2$ unit in AlOO to accept electron density from the Al atom.

## REFERENCES

1. L. Andrews, *J. Amer. Chem. Soc.* **90** (1968) 7368.
2. L. Andrews, *J. Chem. Phys.* **50** (1969) 4288.
3. L. Andrews, *J. Phys. Chem.* **73** (1969) 3922.
4. L. Andrews, *J. Chem. Phys.* **54** (1971) 4935.
5. D. A. Hatzenbühler and L. Andrews, *J. Chem. Phys.* **56** (1972) 3398.
6. R. R. Smardzewski and L. Andrews, *J. Chem. Phys.* **57** (1972) 1327.
7. D. A. Hatzenbühler, R. R. Smardzewski, and L. Andrews, *Appl. Spectrosc.* **26** (1972) 479.
8. L. Andrews and R. R. Smardzewski, *J. Chem. Phys.* **58** (1973) 2258.
9. R. R. Smardzewski and L. Andrews, *J. Phys. Chem.* **77** (1973) 801.
10. L. Andrews, J. T. Hwang, and C. Trindle, *J. Phys. Chem.* **77** (1973) 1065.
11. B. S. Ault and I. Andrews, *J. Chem. Phys.* **62** (1975) 2312.
12. L. Andrews, E. S. Prochaska, and B. S. Ault, *J. Chem. Phys.* **69** (1978) 556.
13. M. J. Zehe, D. A. Lynch, Jr., B. J. Kelsall, and K. D. Carlson, *J. Phys. Chem.* **83** (1979) 656.
14. B. J. Kelsall and K. D. Carlson, *J. Phys. Chem.* **84** (1980) 951.
15. L. V. Serebrennikov, S. B. Osin, and A. A. Maltsev, *J. Mol. Struct.* **81** (1982) 25.
16. S. M. Sonchlk, L. Andrews, and K. D. Carlson, *J. Phys. Chem.* **87** (1983) 2004.
17. D. W. Smith and L. Andrews, *J. Chem. Phys.* **60** (1974) 81.
18. R. D. Spratley, J. J. Turner, and G. C. Pimentel, *J. Chem. Phys.* **44** (1966) 2063.
19. A. Arkell and I. J. Schwager, *J. Amer. Chem. Soc.* **89** (1967) 5999.
20. S. P. So, *Chem. Phys. Lett.* **82** (1981) 370.
21. T. H. Dunning, Jr., *J. Chem. Phys.* **53** (1970) 2823.
22. T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry,* ed. H. F. Schaefer III (Plenum Press, New York, 1977), vol. 3.
23. S. P. So, *J. Chem. Soc., Faraday Trans. 2* **77** (1981) 213, and references cited therein.
24. S. W. Benson and J. H. Buss, *J. Chem. Phys.* **27** (1957) 1382.
25. H. S. Johnstone, E. D. Morris, and J. van Bogaerde, *J. Amer. Chem. Soc.* **91** (1969) 7712.
26. D. D. Wagmen and D. Garvin, *Provisional Thermodynamic Data Sheets for ClO and ClOO* (Natl. Bur. Std., Washington, 1974).
27. M. A.A. Clyne, D. J. McKenney, and R. T. Watson, *J. Chem. Soc. Faraday I* **71** (1975) 332.
28. A. D. Walsh, *J. Chem. Soc.* (1953) 2296.
29. V. E. Bondybey, *J. Phys. Chem.* **86** (1982) 3396, and references cited therein.

30. R. S. Grev and H. F. Schaefer III, *J. Chem. Phys.* **80** (1984) 3552.
31. D. L. Michalopoulos, M. E. Geusic, P. R. R. Langridge-Smith, and R. E. Smalley, *J. Chem. Phys.* **80** (1984) 3556.
32. D. J. Fox, D. Ray, P. C. Rubesin, and H. F. Schaefer III, *J. Chem. Phys.* **73** (1980) 3246.
33. J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta* **20A** (1964) 819.
34. G. Herzberg, *Spectra of Diatomic Molecules,* Van Nostrand, New York (1963).

## SAŽETAK

### Struktura i kemijsko vezanje u aluminijum dioksidu

*S. P. So*

Provedeni su *ab initio* računi elektronske i geometrijske strukture $AlO_2$ korištenjem osnovnog skupa funkcija DZ + P. Rezultati pokazuju da je savijeni AlOO izomer stabilniji od simetričnog, savijenog OAlO izomera. Veza Al—O ima znatan kovalentni karakter.