A Molecular-orbital Treatment of Bonding in Dioxygen Difluoride and Hydrogen Peroxide

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To account for the long AF (A=O, S or N) and short AO or SS bonds in O_2F_2, S_2F_2, and FNO, qualitative valence bond,[1] molecular orbital,[2-5] and non-pairing spatial orbital[6] descriptions have been proposed. In this note we report some results of VESCF molecular orbital calculations† for O_2F_2 and O_2H_2. These studies have been made to test the hypothesis that the differences in AO and AY (Y=F or H) bond properties arise from varying degrees of interaction of oxygen $2p$ π-electrons with the AY σ-bond of the classical valency structures

$$Y-\overset{..}{\underset{..}{A}}-\overset{..}{\underset{..}{A}}-Y \quad \text{or} \quad Y-\overset{..}{\underset{..}{N}}=\overset{..}{\underset{..}{O}}-.$$ Such interactions

will lengthen the AY bond and shorten the AO bond.[7] This hypothesis may be contrasted with the recent molecular orbital model of Spratley

and Pimentel.[5] Their model requires significant donation of charge from fluorine to the antibonding $\bar{\pi}_{00}^*$ orbital (π_{00}^* in their notation) of O_2 (or $\bar{\pi}_{NO}^*$ in NO), otherwise no AF bond will be formed. However, the σ_F-orbital must interact with both $\bar{\pi}_{00}$ and $\bar{\pi}_{00}^*$ since these orbitals belong to the same irreducible representation of a YAO-type system.[7,8] Our results[9] indicate that, for O_2F_2, such interactions occur to a considerable extent in the principal OF bonding molecular orbitals. The molecular orbitals of O_2H_2 that are OH bonding are predominantly localised OH bond orbitals. When interaction of s_H with $\bar{\pi}_{00}^*$ occurs, the OO antibonding character of the occupied molecular orbitals is small.

TABLE

Molecule[a]	R_{OO}, R_{OY}[b] (Å)	$P_O^{\bar{\pi}}$	P_{OO}[c](P_{OO}^σ, $P_{OO}^\pi + P_{OO}^{\bar{\pi}}$)	P_{OY}[b,d](P_{OY}^σ, $P_{OF}^\pi + P_{OF}^{\bar{\pi}}$)
(1) O_2H_2	1·217, 0·95	1·98	1·25 (0·99, 0·26)	0·97 (0·97, —)
(2) O_2H_2	1·35, 0·95	2·00	1·07 (0·99, 0·08)	0·98 (0·98, —)
(3) O_2H_2	1·475, 0·95[e]	2·00	1·03 (0·99, 0·04)	0·99 (0·99, —)
(4) O_2H_2	1·475, 0·95[e]	1·90	0·90 (0·96, —0·06)	0·85 (0·85, —)
(5) O_2F_2	1·217, 1·575[f]	1·25	2·34 (0·98, 1·36)	0·66 (0·50, 0·16)
(6) O_2F_2	1·217, 1·575[f]	1·64	2·09 (0·99, 1·10)	0·95 (0·81, 0·14)
(7) O_2F_2	1·35, 1·50	1·89	1·67 (0·99, 0·68)	1·06 (0·94, 0·12)
(8) O_2F_2	1·475, 1·42	1·95	1·43 (0·97, 0·46)	1·15 (0·97, 0·18)

[a] $\angle$OOY = 90°; dihedral angle = 90° except for (4) $\angle$OOH = 90°; dihedral angle = 120°; and (5) $\angle$OOP = 120°; dihedral angle = 90°. [b] Y = F or H. [c] Total OO bond order. [d] Total OY bond order. [e] A. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, 1962, **36**, 1311. [f] Ref. 4.

† The method of calculation is basically that of ref. 7 with modifications (*e.g.*, J. J. Kaufman, *J. Chem. Phys.*, 1965, **43**, S152), to the $F_{\mu\mu}$ matrix elements, to allow for the presence of more than one orbital per atomic centre. It includes all valence electrons except 2s-lone pairs. K. Ohno's procedure (*Theoret. Chim. Acta*, 1964, **2**, 219) for calculating $\beta_{\mu\nu}^{core}$ has been used. The notation $\bar{\pi}$ denotes an atomic ($2p$) or bond orbital of local π-type symmetry lying in the YOO plane.[7] P_{AY}^σ, $P_{AY}^{\bar{\pi}}$ and P_{AY}^π are Coulson bond orders involving AY atomic orbitals with local σ-, π-, or $\bar{\pi}$-symmetry.

As criteria of delocalisation of oxygen $2p\bar{\pi}$-electrons and of bond length, we have calculated charges $(P_O^{\bar{\pi}})$ and bond orders. Our results (see Table) suggest that extensive delocalisation of oxygen $2p\bar{\pi}$-electrons accounts for the long weak OF and short strong OO bonds in O_2F_2. Such delocalisation is small for O_2H_2. Delocalisation is favoured in O_2F_2 for the following reasons: (a) fluorine is more electronegative than hydrogen, (b) an OF single bond (e.g., 1·42 Å in F_2O[10]) is longer than an OH single bond (0·95 Å) and therefore the OF σ-bond overlap integral is smaller. Consequently the σ_{OF}- and σ_{OF}^*-orbitals lie closer in energy to the $\bar{\pi}_O$-orbital than do the σ_{OH}- and σ_{OH}^*-orbitals. These factors assist greater interaction of oxygen $2p\bar{\pi}$-electrons with the OY bond of O_2F_2 than of O_2H_2.

The degree of delocalisation was investigated for different molecular geometries (see Table). Our conclusions are qualitatively insensitive to the variation in OF length and OOY angles. The OO bond order for O_2F_2 is greater than for O_2H_2 for each OO distance, and the OO bond orders[4] demanded by the experimental geometries (2 for O_2F_2, 1 for O_2H_2) are only reasonably reproduced by the calculations [(3), (4), (5) and (6) in Table] for the experimental bond distances.

[1] L. Pauling, "Nature of the Chemical Bond" 3rd Ed. 1960, Cornell University Press, Ithaca, New York, p. 345.
[2] J. F. A. Williams, Tetrahedron, 1962, 18, 1477.
[3] R. D. Brown, private communication.
[4] R. H. Jackson, J. Chem. Soc., 1962, 4585.
[5] R. D. Spratley and G. C. Pimentel, J. Amer. Chem. Soc., 1966, 88, 2394.
[6] J. W. Linnett, J. Amer. Chem. Soc., 1961, 83, 2643; J. Chem. Soc., 1963, 4663; J. W. Linnett and R. M. Rosenberg, Tetrahedron, 1964, 20, 53.
[7] R. D. Brown and R. D. Harcourt, Austral. J. Chem., 1965, 18, 1115.
[8] R. D. Harcourt, Theoret. Chim. Acta., 1964, 2, 437.
[9] R. D. Harcourt and S. J. Turner, unpublished results.
[10] J. A. Ibers and V. Schomaker, J. Phys. Chem., 1953, 57, 699.