Experimental Bond Orders

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The Significance of Ionic Bonding in Sulfur Dioxide: Bond Orders from X-ray Diffraction Data**

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Lewis diagrams and the octet rule[1] are central concepts in chemistry. Hypervalent molecules break the octet rule because they contain atoms with more than four electron pairs in their valence shell.[2] To describe them with the Lewis model requires hybridization schemes involving d orbitals (sp^3d or sp^3d^2 hybrids).[3,4] The problem is that the formation of these hybrid orbitals requires large promotion energies.[5] Therefore, the significance of ionic resonance diagrams, which obviate the need for hypervalency, has long been discussed.[4]

In this context, the electronic structure of SO_2 has been controversial. SO_2 can be described as a hypervalent molecule (Figure 1, left). Apart from d-orbital hybridization, multiple covalent bonding in SO_2 may be explained by three-center p_π–p_π interactions of the sulfur $3p_\pi$ orbital with non-bonding oxygen p_π electrons (this interpretation goes back to Ref. [6]). However, other non-hypervalent ionic resonance structures can be formulated that preserve the octet rule (Figure 1).

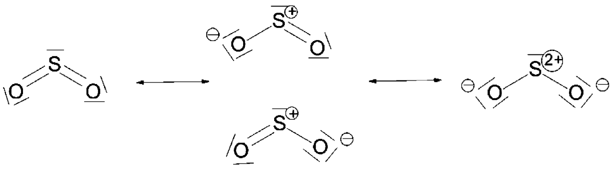

Figure 1. Lewis resonance structures of SO_2.

The neutral Lewis structure is thought to be dominant, as the S–O bond length in SO_2 is shorter than that in sulfur monoxide, SO (1.4299(3) Å in SO_2 from this study, compared to 1.481 Å for SO[7]). The bond dissociation energy is also higher in SO_2 than in SO (547.3(8) kJ mol^{-1} vs. 517.1(8) kJ mol^{-1} [8]). Furthermore, O_3 and O_2, which are valence-isoelectronic with SO_2 and SO, have no available d orbitals, so they cannot be hypervalent, implying bond orders no higher than 1.5 and 2.0, respectively. This is consistent with the fact that the O–O distance in O_3 (1.2717(2) Å[9]) is longer than in O_2 (1.15(8) Å,[10] 1.207 Å[7]), in direct contrast with SO_2 relative to SO. This could support the notion that multiple covalent bonding is significant in SO_2. Indeed, a large number of textbooks[11,12] adhere to this conclusion; for example, in ref. [12] it is stated that the S–O bond order is "at least 2".

The simple empirical analysis above is in sharp contrast to the fact that computational studies have found significant ionic contributions to the S–O bond, and very little sulfur d-orbital participation.[13] Today, there is agreement among theoreticians that the role of d orbitals in the formation of bonds involving second and higher row elements is predominantly one of polarization functions, not of hybridization involving d orbitals.[5,14] In fact, the shorter and stronger bonds in SO_2 compared to SO (which is formally a double bond) support the conclusion that there are significant non-covalent contributions to the bonding. Indeed, calculations employing the electron localization function have shown that the polarity of a bond only depends on the electronegativity differences of the bonded atoms, so that molecules formerly classified as being hypervalent can be readily described with various ionic resonance structures.[15] So from a computational viewpoint, hypervalency is avoided by introducing ionic bonds.

Experimentally, it has hitherto been difficult to obtain information on bond order. A low S–O bond order around 1.5 has been experimentally proposed for SO_2 based on low-energy particle-accelerator measurements.[16] Otherwise, information concerning electrons in bonds comes from the analysis of the topology of electron densities from high-resolution X-ray diffraction experiments.[17] This method uses the electron density as a bridge to understand bonding, rather than directly using the orbitals or density matrices from which the notions of bond order ultimately originate.[18] Nonetheless, such X-ray electron-density investigations do not support hypervalency for second-row elements,[19] even if the atom is hypercoordinated.[20] For example, studies on imide analogues

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of SO_2 have shown that the short S–N bonds are not due to multiple covalent bonding, but to electrostatic attraction of the positively charged sulfur and negatively charged nitrogen atoms.[21]

Herein, we present for the first time bond-order information derived from an experiment, namely from high-resolution low-temperature X-ray diffraction on crystalline SO_2. For comparison, we also give experimentally derived S–O bond orders for the sulfonyl (O_2SR_2) group in compound **1** (Figure 2b). SO_2 was crystallized in situ on the diffractometer at 118 K, below its melting point; compound **1** was measured at 100 K.[22]

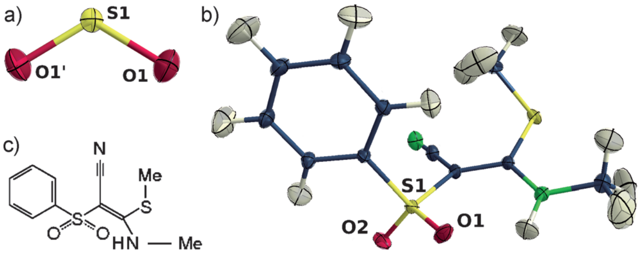

Figure 2. Molecular structures from the X-ray diffraction experiment of a) SO_2 and b) compound **1**, with atom numbering in the SO_2 group; anisotropic displacement parameters (ADPs) at a 50% probability level; ADPs freely refined for the hydrogen atoms. Bond lengths [Å]: S1–O1 1.4299(3) for SO_2, S1–O1/2 1.4449(3)/1.4420(3) for **1**. AIM[17] bond path lengths [Å]: S1–O1 1.4322(33) for SO_2, S1–O1/2 1.4460(31)/1.4444(64) for **1**. Angles [°]: O1-S1-O1′ 117.16(3) for SO_2, O1-S1-O2 117.87(2) for **1**. c) Structural formula of compound **1**.

To derive these novel bonding descriptors, a combined Hirshfeld atom refinement and X-ray constrained wavefunction fitting was applied for the first time (termed "X-ray wavefunction refinement"). In the first step of the X-ray wavefunction refinement, positions and anisotropic displacement parameters (ADPs) were refined for all atoms, including hydrogen atoms, using an ab initio wavefunction and Hirshfeld atom partitioning.[23] A BLYP/cc-pVTZ wavefunction was used, with the molecules embedded self-consistently in a field of their own atomic charges and dipoles. Once the geometric parameters were refined, the orbital parameters in the wavefunction were fitted to the X-ray data.[24] The obtained wavefunction, which included all of the measured information, was then analyzed using published techniques (delocalization index δ,[25] Roby bond index τ,[26] electron localizability indicator ELI,[27] atoms-in-molecules (AIM) approach[17]) to provide the bonding information that is important to chemists (for details on the experiments and the refinement, see Ref. [22] and the Supporting Information).

Quality controls for the X-ray refinement procedure are provided in the Supporting Information. With respect to a pure electron-density analysis, we find that X-ray wavefunction refinement performs better than a sophisticated multipole model[28] that employs the latest methods (for example, sulfur core contraction/expansion[29] and optimized radial-function parameters for the sulfur atom[30]). It performs better when judged in terms of R values, deformation and residual density maps, fractal dimension distribution analysis of the residual density,[31] and topological electron-density results (bond and atomic properties). The latter are also compared to results from isolated-molecule (density functional hybrid and coupled-cluster methods[32]) and periodic-boundary calculations. Comparison between ADPs from the X-ray wavefunction refinement and from the multipole modeling with values in the literature for other sulfonyl compounds measured at similar temperatures shows that thermal motion is well described in the X-ray wavefunction refinement.[33]

The molecular structures obtained are shown in Figure 2. Owing to crystal symmetry, two identical S–O bonds were observed in SO_2, with a bond distance of 1.4299(3) Å and a bond angle of 117.16(3)°. This is not the case for the sulfonyl group in **1**: O1 has several intra- and intermolecular N–H···O1 hydrogen bonds (Figure 3), but O2 is only involved in weak C–H···O2 contacts (see the Supporting Information for details on the hydrogen bonds). The Lewis structure of the sulfonyl group has four bonds and no lone pair for the sulfur atom, whereas there are two bonds and one lone pair in SO_2. Therefore, to avoid hypervalency, the S–O bond orders in SO_2 need to be 1.5 or less, but they need to be 1.0 or less in compound **1**.

Figure 3a shows the S–O bond orders in SO_2 derived from the X-ray diffraction experiment. The Roby bond index τ and the delocalization index δ differ by nearly 0.3 units. The Roby index is larger because it simultaneously describes both covalent and ionic bonding, unlike δ which represents only covalent character. The Roby index is in fact the magnitude of a two-dimensional bond-index vector (1.57, 0.57) comprised of a covalent (1.57) and an ionic (0.57) bond index. It therefore indicates a significant ionic contribution, compare with examples in Ref. [26]. It is instructive to observe bond-order differences that are due to different bond-order definitions. But despite the differences between τ and δ, the bond orders are around 1.5 and clearly not close to 2, which means that sulfur-atom hypervalency is not present in SO_2.

The ellipticity values ε at the S–O bond critical points can be regarded as an additional indirect measure of bond order. The ellipticity is zero for an isolated C–C single bond, 0.23 for a 1.5-fold C–C bond, and 0.45 for an isolated C–C double bond.[34] For SO_2, $\varepsilon(\text{S1–O1}) = 0.09(2)$; for compound **1**, $\varepsilon(\text{S1–O1/2}) = 0.05(7)/0.10(2)$. This confirms that the S–O bonds are between a single and a 1.5-fold bond, which is consistent with ionic Lewis resonance formulas. The AIM[17] atomic charges in Figure 3a, though known to be generally elevated, also support the view that the ionic bond description prevails, with the oxygen atoms drawing electrons from the sulfur atom.

The ELI plot for SO_2 (Figure 3c) shows regions where electron pairs are localized. There are only two oxygen lone pairs per atom, but each lone pair basin is populated with 2.8 to 3.0 e; also the sulfur lone pair is populated with 2.8 e, which is more than expected for one electron pair. This is consistent with an ionic description. However, the large lone pair populations mean that the ELI and Lewis pictures cannot be completely reconciled. The topology of the ELI suggests that an ionic Lewis structure with two highly populated (but not three) lone pairs at the oxygen atoms is the correct explanation of the electronic situation in SO_2. Because of

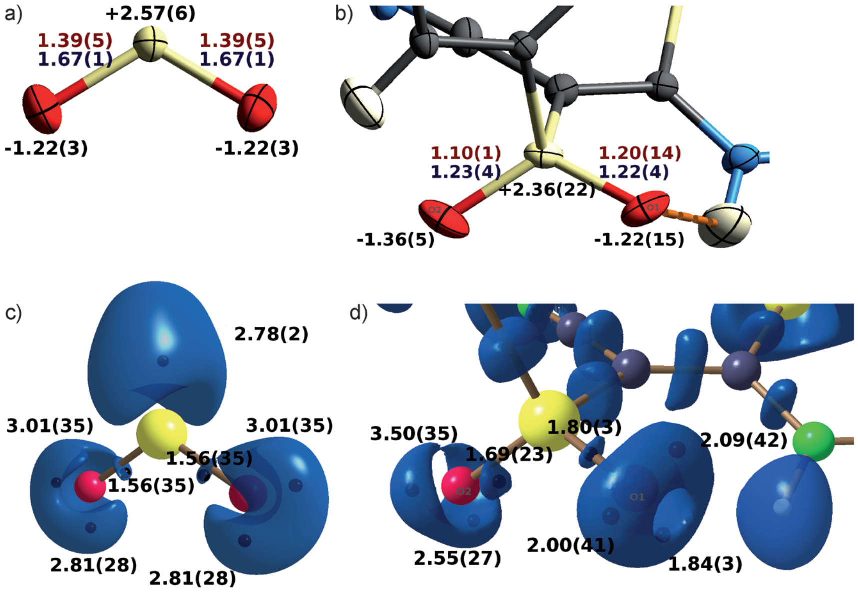

Figure 3. Experimentally derived AIM[17] charges (black, in e) and experimentally derived bond indices (first line/dark red: delocalization index;[25] second line/dark blue: Roby bond index[26]) for a) SO_2 and b) the sulfonyl group; experimentally derived ELI[27] valence basin populations (in e) for c) SO_2 and d) the sulfonyl group, black spheres below the transparent ELI isosurfaces indicate the positions of the basin attractors (that is, maxima); isovalue in (c): ELI = 1.475, isovalue in (d): ELI = 1.445 around the S—O bond attractors and ELI = 1.550 around the lone-pair attractors. The procedure to estimate the experimental errors is described in the Supporting Information.

the excess lone-pair populations, the S—O ELI bond basins are weakly populated with only 1.6e, which is less than expected for a single bond. It is a usual feature in the topology of the ELI that polar bonds are populated weakly in favor of adjacent lone pairs (compare with Ref. [27]), but the effect is unusually pronounced here.

In the sulfonyl group in **1** (Figure 3b) the S—O bond orders from the two methods are closer, namely between 1.1 and 1.2. The smaller value indicates a sulfur atom that is close to non-hypervalent (bond order of 1.0). However, as the values are above 1.0, the nature of the bond lies between the hypervalent sulfonyl Lewis structure with one double and one single bond, and the non-hypervalent sulfonyl structure with two single bonds. Thus, for O1 there are three lone pairs, indicated by three ELI valence attractors (that is, maxima) below the ELI isosurface (Figure 3d). Moreover, the shape of the lone pairs of O1 and O2 has changed toward a ring-like arrangement around the oxygen atom, similar to the shape of the three lone pairs around a covalently bonded fluorine or chlorine atom,[15,35] and is consistent with the Lewis picture where the weight of the diagram with three lone pairs is stronger (compare this with the typical cashew-nut-like shape of the ELI isosurface for the two lone pairs above the oxygen in SO_2 in Figure 3c). For O2, there are still only two lone pairs, but they are on the verge of becoming three. The topological difference between O1 and O2 might be attributed to the fact that O1 is involved in intra- and intermolecular interactions (see above), whereas O2 is only weakly involved.

To investigate the origin of the lone-pair effects in compound **1** further, theoretical isolated-molecule calculations were performed for comparison (see Ref. [32] and the Supporting Information for details). Although the difference of the shapes of the lone pairs in the ELI picture between the sulfonyl group and SO_2 is the same as that discussed, a significant difference between experiment and theory is that there are only two lone pairs for O1 in compound **1**.

The numerical differences between X-ray wavefunction and theoretical results are rather small; ELI valence populations vary by 0.1 to 0.5e and bond orders by a maximum of 0.1, which is within about three times the experimental error, and is about the same as the difference between the two theoretical methods with and without electron correlation (see the Supporting Material for a detailed comparison).

It seems that intermolecular interactions and electron correlation have a non-negligible influence on the topology and to a lesser degree on the values of the bond descriptors in the SO_2 group. For a small molecule like SO_2, it might be feasible to account for both crystal-field and electron-correlation effects with a purely theoretical calculation. However, for larger compounds with even heavier atoms than in compound **1**, X-ray wavefunction refinement is at present the only way to obtain reliable and rapid access to wavefunctions that include the effects of both electron correlation and intermolecular interactions. Moreover, it provides superior electron-density modeling at an accurately determined experimental geometry, and it gives access to a broad variety of new methods for the characterization of bonds.

In summary, bond orders derived from an X-ray wavefunction refinement clearly show that ionic bonding and not hypervalency prevails in the description of the S—O bonds of SO_2 and the sulfonyl group. The bond orders are 1.5 and 1.2 in SO_2 and the sulfonyl group, respectively. Thus, electrostatic forces (and not multiple covalent bonding) contribute more to the S—O bond shortening. These conclusions must be accounted for in new revisions of widely used textbooks, especially since bond distance correlations are misleading in the case of SO_2. The possibility of establishing bond orders using X-ray wavefunction refinement is therefore of utmost importance in resolving fundamental chemical problems. It seems likely that in the future bond orders can be delivered along with bond distances from routine X-ray structure determinations.

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