

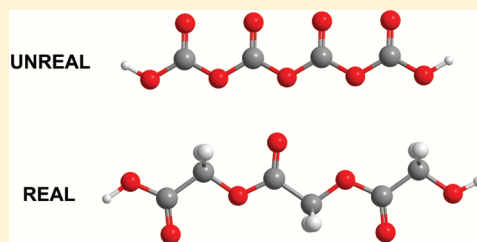
Atomic Volume as a Descriptor for Carbon Electronic Structure and Stability

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Supporting Information

ABSTRACT: Electron density at the carbon atom is a significant factor determining the stability of molecules, but it is difficult to quantify. Using the Atoms in Molecules (AIM) quantum theory, we calculated the atomic charges and volumes of carbon atoms in highly oxidized compounds. The two parameters are shown to be good quantitative descriptors of electron depletion and can be used as an indicator for stability/reactivity of such compounds.



Any organic chemist intuitively understands that organic compounds in which a carbon atom is attached to “too many” electron-withdrawing groups will be reactive and ultimately unstable. Surprisingly, a quantification of this simple phenomenon remains absent. In this paper, we propose a method for quantifying this effect through the use of atomic charges and volumes calculated by the Atoms in Molecules (AIM) quantum theory.¹

The effect of oxygen as a strongly electronegative atom on an adjacent carbon atom can be illustrated by the comparison of polyglycolic acid $-(\text{OCH}_2\text{C}(\text{O}))_n-$, a biodegradable polymer that is widely used in medicine, and polycarbonic acid $-(\text{OC}(\text{O}))_n-$ (polymeric CO_2), which does not exist. The difference is a single methylene group in the main chain repeating unit. When present to separate the two ester groups the structure is reactive (easily hydrolyzable in this case) but stable, whereas when it is not present the ester groups cannot remain joined together in a stable structure under normal conditions. The two adjacent ester groups linked in a “tail-to-tail” ($\text{HOOC}-\text{COOH}$) fashion are stable in oxalic acid, which is a structural isomer of a “head-to-tail” carbonic acid dimer ($\text{HCOO}-\text{COOH}$) that does not exist.

These two examples deal with the border between stable (existent) and unstable (unreal) structures, and the same trend can be seen in biodegradable polymers, particularly polyesters, where stability, as reflected in lower degradation rates, parallels a lower average oxidation state of the main-chain carbon atoms.^{2,3} A higher content of alkyl sections in the chain will result in a less degradable (more stable) polymer. The upper limit of this direction is polyethylene $-(\text{CH}_2)_n-$, which is not biodegradable. The fact that it becomes partially biodegradable when it is partially oxidized is at the core of the oxo-degradable plastic technology, i.e., the commercial application of metal ion catalysts to promote oxidation, thus making commodity polymers such as polyethylene (bio)degradable.

In our previous work, we used computational methods to study stable and unstable highly oxidized oligomers, and we were

able to show that replacing C–O bonds with C–C bonds (e.g., poly(oxalic acid) vs poly(carbonic acid)) as well as by insertion of methylene groups in the main chain results in significant stabilization.⁴ Traditional quantum-chemical modeling implemented in our previous work yields stabilities based on energy criteria, but it lacks explanatory power.

Carbon dioxide is the most oxidized form of carbon, and its polymer forms do not exist under normal conditions. However, it was shown that under high pressures (1–80 GPa) the CO_2 molecule can bend from its linear form and the carbon atom starts transforming from a divalent to a trivalent form and eventually ends with four valencies.⁵ By this method, a quartzlike solid with a tetrahedral spatial organization and an amorphous glass have both been obtained.^{6,7} Linear structures of CO_2 have not been detected. A real compound that comes closest to linear polymeric CO_2 under normal conditions is di-*tert*-butyl tricarbonate with a formal carbonic acid trimer between the bulky end groups.⁸

Polyoxalic acid has never been reported, but a polyoxalate chain has been shown to be stable when coordinated to zinc ions and embedded in a well-chosen scaffold.⁹ Very recently, a copper ion catalyzed method was reported for the direct conversion of CO_2 to oxalate.¹⁰

A logical examination of the question as to why increasing levels of oxidation lead to less stable carbon centers suggests that it is related to depletion of the electron density in the vicinity of the carbon atom. Thus, it should be possible to correlate stability to the molecular electron density.

To examine this hypothesis, we performed a series of ab initio quantum chemical calculations of closely related structures shown in Table 1. The Hartree–Fock method was used in conjunction with basis set 6-31G(d). For some species, the calculations were also performed on the MP2/6-31++G(d,p)

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Table 1. Structures Studied

compd/abbrev	X	Y	Z
formic acid/fa	H	OH	O
acetic acid/aa	CH ₃	OH	O
glycolic acid/ga	CH ₂ OH	OH	O
oxalic acid/oa	COOH	OH	O
urea/u	NH ₂	NH ₂	O
thiourea/tu	NH ₂	NH ₂	S
isobutene/ib	CH ₃	CH ₃	CH ₂
carbonic acid/ca	OH	OH	O
ca trimer/ca3	OCOOH	OCOOH	O
ca decamer/ca10	O(COO) ₄ H	O(COO) ₅ H	O
caNN	OH	OH	NH
caSS	OH	OH	S
caN	NH ₂	OH	O
caS	SH	OH	O

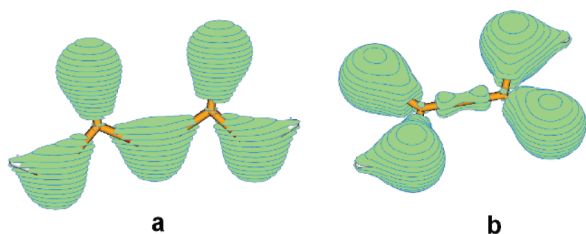


Figure 1. Representations of electron density in (a) the dimer of carbonic acid (HOC(O)OC(O)OH) and (b) oxalic acid (HOC(O)-C(O)OH), at the same contour level. The electron density along the C–C bond allows carbon to retain more of its electrons than when bonded to the electronegative oxygen atoms.

level. Computational details are given in the Supporting Information. We first calculated molecular electron densities and examined their distributions. An illustrative example is given in Figure 1 showing electron density at the same contour level for the dimer of carbonic acid (**ca2**) and oxalic acid (**oa**). The major difference is the electron density surrounding the carbon atoms: in **ca2** virtually all electron density is continuous with the adjacent oxygen atoms, whereas in **oa** the density, which is located along the bond, is shared by the two carbon atoms. This suggests a qualitative difference in the distribution of carbon atom electron density.

To rationalize the meaning of this observation for the electronic structure, we proceeded to assign electron density to individual atoms in the molecules. We employed the Atoms in Molecules (AIM) quantum theory due to its elegant and intuitive principle for distributing electron density by determining zero flux surfaces. These partition the space of a molecule into a set of monatomic regions that correspond to atoms and recover their measurable properties. The calculation is based on wave function coefficients as input for AIM analysis from which we obtained critical bond point (BCP) positions and properties as well as atom charges, volumes, and energies.

Detailed results from calculations are given in the Supporting Information. First, BCP, the point on the bond path where both

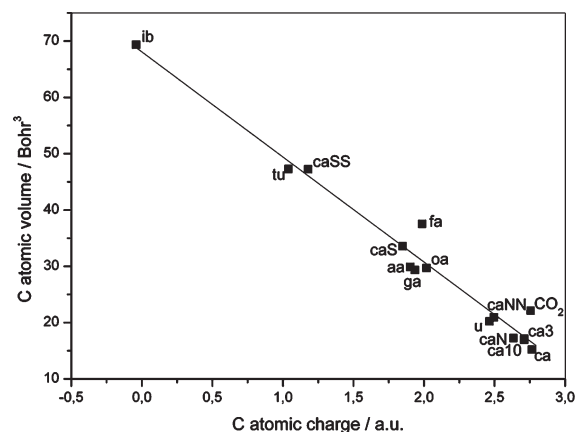


Figure 2. Correlation of carbon atom charge and volume obtained by Atoms in Molecules (AIM) quantum theory in examined compounds. Please note that carbon atom volumes below 18 bohr³ correlate with unstable structures. (linear fit: $y = -18.663x + 68.082$, $R^2 = 0.9687$).

adjointed atomic basins meet, were examined; however, no systematic trends could be found distinguishing stable (real) and unstable (unreal) structures. Surprisingly, the BCP position did not shift substantially even when very different groups were connected to the carbon. This is contrary to the observation of Grabowski et al. for substituted ethylenes and acetylenes.^{11–13} The electron density in the BCP as well as the ellipticity, an index of the concentration of charge in a plane, also showed no systematic trends. Ellipticity, however, has been shown to be strongly influenced by large charge.¹⁴

The next step was to examine the atomic charges and volumes. Ditttrich et al. showed a high level of transferability of AIM-derived atomic volumes and charges in the peptide bond in solid state.¹⁵ In our case, atoms attached to the central carbon atom showed little variation in their charges and volumes, both being overwhelmingly influenced by the type of atom. The changes in both charge and volume, however, became significant at the central carbon atom and followed the electronegativity of the atoms involved. The correlation of carbon atom volume vs charge is shown in Figure 2. In cases where the carbon atom was surrounded by the most electronegative oxygen atoms (**ca**, **ca3**, **ca10**, and **CO₂**), its AIM-calculated charge was approximately +2.7 au and the atomic volume 20–15 bohr³. Interestingly, the C atom volume in **CO₂** is above the linear correlation, which could be attributed to the linearity of the molecule (*sp* hybridization) that is likely to play a role in the stability of **CO₂**. The C atom volume gradually increases and the charge decreases as oxygen atoms are replaced by the less electronegative nitrogen atoms (**caN**, **u**, **caNN**), hydrogen (**fa**), and carbons (**oa**, **ga**, **aa**) and finally by the large and electropositive (vs carbon) sulfur atoms (**caS**, **caSS**, **tu**). To examine the validity of the correlation at the opposite extreme of the atomic charge/volume range, we included isobutene (**ib**) in which the central carbon atom is surrounded by carbon atoms of equal electronegativity where minimal charge transfer is anticipated. The correlation shown in Figure 2 shows that calculated carbon atom charges and associated volumes follow a predictable and additive effect of neighboring groups that coincides with the stability/reactivity. High electron depletion is associated with small atomic volumes and unstable (unreal) structures, whereas medium depletion results in charge separation associated with reactive real molecules. Due to its greater variability, we suggest AIM-calculated

atomic volume rather than charge as the most sensitive descriptor for the electronic strain of oxidized carbons. The same conclusions were reached using the MP2/6-31++G(d,p) level (Supporting Information).

Another interesting conclusion can be derived from the fact that BCP positions did not shift substantially even when the atomic volumes of the central C atom differed significantly. This indicates that the main contribution to the variations in atomic volume comes from directions that are not associated with the chemical bond.

Further confirmation for the validity of the charge/volume correlation was found in carbon atom energies $E(C)$ (data in the Supporting Information). The energy of an atom is an expectation value of the Hamiltonian integrated over the space corresponding to that particular atom.¹⁶ Obtained $E(C)$ values for different structures followed the same linear trend as atomic volumes, but in reverse: with the lowest energy in **ib** (most stable) and with the highest values in highly oxidized species (e.g., **ca**) (most unstable).

Stability (a thermodynamic quantity) for a series of closely related species can be related to reactivity via the linear free energy relationship, which states that less stable species are more reactive, increasing the potential biodegradability in the case of polymers.

The electronic environment of an atom is a prominent factor determining NMR chemical shifts; however, as anticipated¹⁷, no correlation could be found between ¹³C shifts and atomic charges (Table 2, Supporting Information), showing NMR as an inappropriate experimental method to verify our results. Insensitivity of chemical shifts to the level of oxidation can be explained by the fact that the electric field gradient at the nucleus is not sensitive enough to the outer shell electron density.

Based on our results, we conclude that highly oxidized organic compounds become unstable due to the severe depletion of electron density at the carbon atom. This leads to an unsustainable situation where the atom can formally lose as much as 2.7 of its four outer shell electrons. Atomic volumes and corresponding charges as defined by Bader's atoms in molecules quantum theory offer a practical tool to quantitatively evaluate this depletion, which was found to correlate well with the stability of compounds containing electron-deficient carbon centers. The HF/6-31G(d)-calculated carbon atomic volume below 18 bohr³ indicates instability. This relationship, although intuitively very well understood in chemistry, is otherwise difficult to determine.

■ ASSOCIATED CONTENT

Supporting Information. Computational details and detailed calculated bond and atomic properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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