First-principles investigations on C$_5$O$_5^{-}/^{0}$ and C$_6$O$_6^{-}/^{0}$ oxocarbons

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Comprehensive first-principles calculations on the geometrical and electronic properties of C$_5$O$_5^{0}$ and C$_6$O$_6^{0}$ oxocarbons have been performed in this work. Both C$_5$O$_5$ monoanion and C$_6$O$_6$ neutral are found to possess perfect planar pentagonal structures at their ground states D$_{5h}$ C$_5$O$_5$ ($1^3A^1$) (1) and D$_{5h}$ C$_6$O$_6$ ($1^3A^1$) (2), while C$_5$O$_5^-$ and C$_6$O$_6^-$ appear to favor the slightly distorted quasi-planar C$_5$O$_5^-$ ($2^3A_1$) (3) and C$_6$O$_6^-$ ($2^3A_1$) (4), respectively. Adaptive natural density partitioning (AdNDP) analyses clearly reveal the σ- and π-bonding patterns of the monocyclic C$_5$O$_5^{0/-}$ oxocarbons (n=5 and 6). The adiabatic detachment energies (ADEs) and low-lying vertical detachment energies (VDEs) of the monoanions have been calculated at the coupled cluster level with triple excitations (CCSD(T)), with ADE = 3.723 and VDE = 3.776 eV for C$_5$O$_5$ and ADE = 3.629 eV and VDE = 3.679 eV for C$_6$O$_6$. The first excited states of the neutrals are predicted to have the approximate term values of T$_1$ = 1.08 eV ($^{2}A_1$) for C$_5$O$_5$ and T$_1$ = 1.22 eV ($^{2}B_1$) for C$_6$O$_6$. The predictions made in this work may help facilitate experimental characterizations of C$_5$O$_5$ and C$_6$O$_6$ monoanions.

1. Introduction

Oxocarbons C$_n$O$_n$ (n = 3–6), the cyclic polymers of carbon monoxide, have attracted considerable attention in the past several decades [1–42]. The well-known C$_5$O$_5^2-$ dianions (n = 3–6) have been extensively studied in chemistry due to their π-aromaticity, capacity as either bridging ligands or building blocks in interesting materials and usefulness in analytical applications [27–42]. In contrast, much less attention has been paid to C$_n$O$_n$ neutrals and C$_n$O$_n^+$ monoanions which started to arouse the curiosity of chemists in the past decade. The main theoretical investigations in this aspect are focused on the unusual electronic structure of C$_5$O$_5$ which was predicted to have a triplet ground state at coupled cluster level with triple excitations (CCSD(T)) [27–31]. This prediction was confirmed in 2012 by photoelectron spectroscopy (PES) measurements coupled with an electrospray ionization (ESI) source of C$_5$O$_5$ clusters generated from squaric acid solution of C$_x$H$_{2x}$, combined with CCSD(T) calculations [32]. Shortly after this report, a comprehensive molecular orbital (MO) analysis for the whole oxocarbon neutral series (CO)$_n$ (n = 2–6) appeared very recently [33]. At the best of our knowledge, limited investigations have been reported for C$_n$O$_n$ monoanions and their neutrals C$_n$O$_n$ (n = 5, 6) [28–42]. Experimentally, C$_5$O$_5$ radical was firstly observed in ESR measurements by oxidation of bis(triphenylphosphine) iminium croconate in 1973 [12]. Trace amounts of C$_5$O$_5$ and C$_6$O$_6$ monoanions in gas phases were observed in mass spectrum in 1999 [41]. C$_6$O$_6$ monoanion was also recently produced from oligomerization of CO on molybdenum anions in 2006 [42]. As a powerful experimental technique, PES can be used to directly probe the electronic states of both monoanions and their neutrals. But only very accurate theoretical calculations at coupled cluster levels are expected to provide reliable theoretical predictions to assign the PES spectra of C$_n$O$_n$ monoanions, as noticed in the case of C$_5$O$_5$ [32]. The ground states of C$_5$O$_5$ (n = 5, 6) neutrals are known to be singlet [17,33]. However, the ground states of C$_6$O$_6$ (n = 5, 6) monoanions and the exited states of their neutrals still remain unknown to date. In this work, we present comprehensive first-principles investigations on the geometrical and electronic structures of C$_5$O$_5^{0/-}$ and C$_6$O$_6^{0/-}$ and predict the low-lying one-electron detachment energies of C$_5$O$_5^-$ and C$_6$O$_6^-$ to facilitate their experimental characterizations. We also provide detailed molecular orbital analyses for C$_n$O$_n^{0/-}$ clusters (n = 5, 6) to help understand their σ- and π-bonding patterns and probe the one-electron detachment channels from C$_n$O$_n$ monoanions to their C$_n$O$_n$ neutrals.

2. Computational methodology

The geometries of C$_n$O$_n$ neutrals and C$_n$O$_n^+$ monoanions (n = 5, 6) were fully optimized at both B3LYP [43–44] and MP2 [45–46] levels with the Dunning’s correlation consistent basis sets (aug-cc-pVTZ) [47] for both carbon and oxygen. Vibrational analyses at
B3LYP level were carried out to ensure that all of the optimized geometries were true minima on potential energy surfaces of the systems. Natural bond orbital (NBO) analyses were performed to gain insight into the bonding characters of these species. In addition, chemical bonding analyses of C5O2\textsuperscript{−}/C0\textsubscript{5} and C6O2\textsuperscript{−}/C0\textsubscript{6} were performed utilizing the recently proposed adaptive natural density partitioning (AdNDP) method\textsuperscript{[48–50]} with the 6-31G basis set. It has been shown that the AdNDP results are not sensitive to the level of theory or basis set used. Molecular visualization was performed using Molekel 5.4\textsuperscript{[51]}. Adiabatic detachment energies (ADEs) were calculated as the energy differences between the anions and the corresponding neutrals at their ground-state structures, while the vertical detachment energies (VDEs) as the energy differences between the anions and their neutrals at the ground-state structures of the anions. CCSD(T)\textsuperscript{[52–54]} single-energy differences between the anions and their neutrals at the MP2 geometries. One-electron detachment energies of the monoanions were also approximated with the outer valence Green function approach (OVGF)\textsuperscript{[55]}. All the calculations in this work were performed using the Gaussian 03 software package\textsuperscript{[56]}.

3. Results and discussion

3.1. Structures and stabilities

The optimized structures of C\textsubscript{n}O\textsubscript{2n} monoanions (n = 5,6) and their neutrals are shown in Fig. 1, with the C–C and C–O bond lengths at both B3LYP and MP2 levels indicated. Both C5O2\textsuperscript{−} (1), monoanion and C5O2 (2), neutral are found to take perfect planar D\textsubscript{5h} structures, while C6O2\textsuperscript{−} (3) and C6O2\textsuperscript{+} (4) possess the slightly distorted quasi-planar C\textsubscript{2v} geometries. The C\textsubscript{2v} conformation of C6O2\textsuperscript{−} (3) is a true minimum on the potential energy surface of the monoanion without imaginary frequencies (see Table 1), while other isomers such as D\textsubscript{3h}, D\textsubscript{3d}, D\textsubscript{2}, C\textsubscript{2}, and C\textsubscript{1} turn out to be transition states or high-order saddle points lying slightly higher than C\textsubscript{2v} C6O2\textsuperscript{−} (3) (by less than 0.16 kcal/mol, see Fig. S1 in Supplementary information). These results indicate that the potential energy surface of C6O2\textsuperscript{−} is very flat and its isomers obtained in Fig. S1 are practically isoenergetic with one another. While the energetically nearly degenerate \textalpha-HOMO (a\textalpha\textsubscript{2u}) and \textalpha-HOMO-1 (b\textalpha\textsubscript{1g}) make it difficult to determine the ground state of C6O\textsubscript{2} theoretically\textsuperscript{[28,31–33]}, the energy gaps between the \textalpha-HOMO and \textalpha-HOMO-1 of C5O\textsubscript{2} and C6O\textsubscript{2} appear to be big enough (60.2 and 69.3 kcal/mol at CCSD(T)/B3LYP, respectively) to ensure that the doublet D\textsubscript{5h} C5O\textsubscript{2} (\textalpha\textsuperscript{2}(\textalpha\textsubscript{2})\textsubscript{2}) (1) and C\textsubscript{2v} C6O\textsubscript{2} (\textalpha\textsuperscript{2}(\textalpha\textsubscript{1g})\textsubscript{3}) (2) are the ground states of the systems without ambiguity. This situation greatly simplifies the theoretical calculations on C5O\textsubscript{2}\textsuperscript{−} and C6O\textsubscript{2}\textsuperscript{−}. The optimized singlet ground states of D\textsubscript{5h} C5O\textsubscript{2} (\textalpha\textsuperscript{2}(\textalpha\textsubscript{1g})\textsubscript{3}) (2) and C\textsubscript{2v} C6O\textsubscript{2} (\textalpha\textsuperscript{2}(\textalpha\textsubscript{1g})\textsubscript{4}) (4) in Fig. 1 well agree with the prediction of Schleyer and coworkers\textsuperscript{[17]}.

As can be seen from Fig. 1, B3LYP and MP2 methods produced similar geometries and bond parameters for the concerned oxocarbons. It is interesting to notice that the periphery C–C bond lengths of the monoanions are systematically shorter than the corresponding values of their neutrals (by about 0.037 Å in average) due to the fact that the extra electron on C5O\textsubscript{2} occupies the totally delocalized bonding \textpi-HOMO of the systems over the oxocarbon rings (see Fig. 3). It is this delocalized multi-center-one-electron \textpi-HOMO that makes C\textsubscript{5}O\textsubscript{2}\textsuperscript{−} monoanions thermodynamically more stable than their C\textsubscript{5}O\textsubscript{2} neutrals. The highly stable C\textsubscript{5}O\textsubscript{2}\textsuperscript{−} dianions are produced with one more extra electron in the \textpi-HOMO of C\textsubscript{5}O\textsubscript{2}. In addition, it is expected that the symmetric ring breathing modes of the neutrals to be excited upon detaching one electron from the monoanions. The calculated symmetrical breathing modes (a\textsubscript{1}) of C5O\textsubscript{2} (2) and C6O\textsubscript{2} (4) have the vibrational frequencies of 1754 cm\textsuperscript{−1} and 1742 cm\textsuperscript{−1} (after the 0.97 scaling) at B3LYP/aug-cc-pVTZ level, respectively, which appear to be 70–80 cm\textsuperscript{−1} lower than the ring breathing frequency of 1824 cm\textsuperscript{−1} calculated for C5O\textsubscript{2} at the same theoretical level\textsuperscript{[32]}.

As demonstrated in Table 1, NBO analysis indicates that C and O atoms in oxocarbons well follow the octet rule with the total Wiberg atomic bond indices of WIBL\textsubscript{c} = 3.87–3.89 and WIBL\textsubscript{b} = 1.93–2.17. The C–C Wiberg bond indices of WIBL\textsubscript{c} = 0.89–0.97 calculated for (1–4) clearly indicate that C–C bonds are typical covalent single bond. We notice the C–C bond indexes (WIBL\textsubscript{c} = 0.97) of the monoanions are clearly higher than their neutrals with WIBL\textsubscript{c} = 0.89–0.90, in consistent with the shorter C–C bond lengths in the monoanions than in their neutrals discussed above.

The C–O Wiberg bond indices with the bond orders of (1–4) show that the C–O bonds in these species. Given the fact that oxygen is more electronegative than carbon, it is easy to understand that O atoms in oxocarbons carry negative net atomic charges (q\textsubscript{o} = −0.37[e] ~ −0.53[e]), while C atoms are positively charged with q\textsubscript{c} = +0.33[e] ~ +0.38[e].

The singlet ground states of C\textsubscript{n}O\textsubscript{2n} neutrals (n = 5,6) have been predicted to be unstable with respect to dissociation to n CO molecules\textsuperscript{[17,29,37]}, Schleyer and coworkers\textsuperscript{[17]} proposed that the exothermicities of C\textsubscript{5+n}\textsuperscript{−} (−25.7 kcal/mol for n = 5 and −31.2 kcal/mol for n = 6 at B3LYP/6-311+G\textsubscript{b} level) in the decomposition reactions (C\textsubscript{5+n} → nCO) rationalize the failures to prepare and to observe these "neutral carbon monoxide oligomers". To evaluate the thermodynamic stabilities of their monoanions, we calculate the energy changes of the following processes at CCSD(T)/B3LYP level at 298.15 K and 1 atm:

\[ n\text{CO} \rightarrow C_n\text{O}_n \rightarrow C_n\text{O}_n^- \quad (n = 4, 5, 6) \]

With zero-point corrections included, ΔE\textsubscript{1} = +53.88, +46.49, and +54.42 kcal/mol, ΔE\textsubscript{2} = −80.49, −86.87, and −85.59 kcal/mol, and the overall ΔE = ΔE\textsubscript{1} + ΔE\textsubscript{2} = −26.61, −40.38 and −31.17 kcal/mol for D\textsubscript{5h} C\textsubscript{5+n} \textsuperscript{−}(\textalpha\textsuperscript{2}(\textalpha\textsubscript{2}))\textsubscript{2}, D\textsubscript{5h} C\textsubscript{5+n} \textsuperscript{−}(\textalpha\textsuperscript{2}(\textalpha\textsubscript{1g}))\textsubscript{1}, and C\textsubscript{2v} C\textsubscript{5+n} \textsuperscript{−}(\textalpha\textsuperscript{2}(\textalpha\textsubscript{1g}))\textsubscript{3} (3), respectively. Obviously, with positive formation energies (ΔE\textsubscript{1}), C\textsubscript{5+n}\textsuperscript{−} neutrals are unstable with respect to dissociations to 4CO, 5CO, and 6CO (in consistent with the prediction of Schleyer and coworkers\textsuperscript{[17]}). However, these unstable neutrals possess huge electron affinities (ΔE\textsubscript{2}) upon one-electron attach-

Fig. 1. Optimized ground-state structures of monocyclic C\textsubscript{5}O\textsubscript{2} (1), C\textsubscript{5}O\textsubscript{2} (2), C\textsubscript{6}O\textsubscript{2} (3) and C\textsubscript{6}O\textsubscript{2} (4) with bond lengths indicated in Å at both B3LYP (in normal mode) and MP2 (in italic mode).
ment, making their monoanions C₅O₂⁻, C₆O₂⁻, and C₆O₆⁻ thermodynamically stable with considerable negative overall formation energies (ΔE). In these monoanions, C₅O₂⁻ appears to be the most favorable species in thermodynamics. Given the fact that monocyclic D₅h C₅O₅ was generated from squaric acid solution of C₄O₄H₂ and characterized in PES measurements [32], it is reasonable to expect that monocyclic C₅O₂⁻ (1) and C₆O₂⁻ (3) to be produced from croconic acid (C₆O₄H₂) and rhodizonic acid (C₅O₄H₂) or their salts (like C₅O₄Na₂ and C₆O₄Na₂) and characterized in PES spectral measurements.

### Table 1

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<th>Symm</th>
<th>State</th>
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<th>( q_o )</th>
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<th>WBLb</th>
<th>WBLc-C</th>
<th>WBLc-O</th>
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<td>D₅h</td>
<td>( ^2A_1 )</td>
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<td>-0.53</td>
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<td>1.93</td>
<td>0.97</td>
<td>1.71</td>
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<tr>
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<td>D₅h</td>
<td>( ^1A_1 )</td>
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<td>-0.37</td>
<td>3.89</td>
<td>2.17</td>
<td>0.90</td>
<td>1.92</td>
</tr>
<tr>
<td>C₆O₂</td>
<td>C₂v</td>
<td>( ^2A_1 )</td>
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<td>-0.50</td>
<td>3.87</td>
<td>1.97</td>
<td>0.97</td>
<td>1.74</td>
</tr>
<tr>
<td>C₆O₂</td>
<td>C₂v</td>
<td>( ^1A_1 )</td>
<td>+0.38</td>
<td>-0.38</td>
<td>3.89</td>
<td>2.17</td>
<td>0.89, 0.90</td>
<td>1.92</td>
</tr>
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Fig. 2. AdNDP \( \sigma \)- and π-bonding patterns of C₅O₂^\(2/-1\) (a) and C₆O₆^\(2/-1\) (b) at the ground state structures of the monoanions, with occupation numbers (ONs) indicated.

### 3.2. AdNDP analyses

In order to understand the bonding nature of these oxocarbon species, we performed detailed chemical bonding analyses for D₅h C₅O₅ \( (^2A_1) \) (1) and C₆O₆ \( (^2A_1) \) (3) using the AdNDP approach [48–50]. As an extension of the natural bond orbital analysis, AdNDP is a very efficient and visual approach to interpretation of the molecular orbital-based wave functions. The current version of the AdNDP program can only deal with closed-shell systems. Therefore, in order to assess chemical bonding in the open-shell C₇O₈ \( n = 5, 6 \) anions, we performed AdNDP analyses on both the closed-shell C₅O₂⁺ and C₆O₂⁺ neutrals \( n = 5, 6 \) at the geometries of their monoanions (see Fig. 2). The AdNDP \( \sigma \)- and π-bonding patterns of C₅O₂ \( n = 5, 6 \) monoanions are shown in Fig. 2 as intermediates between the C₅O₂⁺ and C₆O₂⁺ neutrals with averaged occupation numbers (ONs).

We discuss the results obtained for D₅h C₅O₅ \( (^1A_1) \) (1) first. Of the 51 valence electrons, 20 electrons are for the ten 1c–2e lone-pairs (LPs) on 0 atoms, 10 electrons for the five periphery 2c–2e C–C \( \sigma \) single bonds, and 20 electrons for the five 2c–2e C=O double bonds (in which 10 electrons are for the five 2c–2e C=O \( \pi \) bonds and 10 electrons for the five 2c–2e C=O \( \pi \) bonds). The remaining one extra electron occupies the totally delocalized 5c–1e bonding π-bond with the ON = 1.0|e|. The \( \sigma \)- and π-bonding patterns of C₅O₂⁺ (1) and C₆O₂⁺ (3) are similar with D₅h C₅O₅ \( (^2A_1) \) (1), except that the fact that it possesses a singly occupied 6c–1e π-bond over the molecular plane with the ON = 1.0|e|. We stress here that it is the singly occupied delocalized π-bonds (the π-HOMOs) that makes C₅O₂⁻ (1) and C₆O₂⁻ (3) π-aromatic in nature and provides extra stabilization energies to stabilize these monoanions, similar to the situation in C₄O₄ [27–32].

### 3.3. ADEs and VDEs

Under the single-particle approximation (Koopmans’s theorem), vertical electronic detachments can be viewed as removing one electron from each respective occupied MO of the anion. We performed CCSD(T) single-point energy calculations on the ground states of C₅O₂⁻ \( n = 5, 6 \) and the first two excited states of the neutral at both the B3LYP and MP2 geometries of the monoanions to predict their ADEs and low-lying VDEs. We also calculated the first three VDEs of C₅O₂⁻ and C₆O₂⁻ using the (U)OVGF approach. As shown in Fig. 3a, the HOMO \( (\alpha) \) of D₅h C₅O₅ \( (^2A_1) \) (1) is a typical singly occupied delocalized π MO, while the degenerate HOMO-1 \( (\beta) \) includes two doubly occupied π MOs. One-electron detachment from C₅O₂⁻ results in three electron states for neutral C₅O₂. The first VDE corresponds to detaching one electron vertically from the singly occupied π-HOMO with the final neutral singlet state of \( ^1A_1 \), while the second and third VDEs correspond to detachment of a \( \beta \) or \( \alpha \) electron from HOMO-1 \( (\beta) \) which leads to the final neutral triplet \( ^3A_2 \) and singlet \( ^1A_2 \) state, respectively. As listed in Table 2, C₅O₂ has the calculated first detachment energies of ADE = 3.78 eV and VDE = 3.87 eV at ΤCCSD(T)/B3LYP and ADE = 3.723 eV and VDE = 3.776 eV at ΤCCSD(T)/MP2. This gives an approximate electron affinity value of EA = 3.72–3.78 eV for
C5O5 neutral at CCSD(T). The small ADE–VDE difference (<0.10 eV) well demonstrates the minor structural relaxation from D5h C5O5 (1) to D5h C5O5 (2) (see Fig. 1) upon one-electron detachment. The first 3A2 and second 1A2 excited states of the neutral appear to be very close in energy, with the second and third VDE = 4.951 and 5.181 eV at CCSD(T)//B3LYP and VDE = 4.859 and 5.069 eV at CCSD(T)//MP2, respectively. These values define an approximate term value of \( T_1 = 1.08 \) eV for the first (3A2) excited state of D5h C5O5. This value turns out to be much higher than the corresponding measured term value of \( T_1 = 0.065 \) eV (\(^1\text{A}_\text{g}\)) measured for C4O4 in PES experiments [32]. Interestingly, simple (U)OVGF calculations also produce VDE values well comparable with the more accurate CCSD(T) method at both B3LYP and MP2 geometries (see Table 2). The high pole strengths (>0.87) of the electron detachment channels for C5O5 (and C6O6) strongly suggest that multireference interactions be most likely negligible for the monoanions concerned in this work.

A similar situation occurs to C6O6. As demonstrated in Fig. 3b, the HOMO (\( a_2 \)) of C5O5 (\( a_2 \)) (3) is a typical singly occupied \( \pi \) molecular orbital, while its HOMO-1 (\( b_1 \)) is a doubly occupied \( \sigma \) molecular orbital. One-electron detachment from C6O6 results in three electronic states for C6O6, including 1A1, 3B1, and 1B1 which are responsible for the three PES bands (X, A, and B), respectively. The first one-electron detachment (X) from the singly occupied HOMO (\( a_2 \)) produces the singlet final state of 1A1, with ADE = 3.715 eV and VDE = 3.771 eV at CCSD(T)//B3LYP and VDE = 4.859 and 5.069 eV at CCSD(T)//MP2, respectively. These values produce an approximate electron affinity of \( E_A = 3.62–3.72 \) eV for C6O6 at CCSD(T). The second (A) and third (B) VDEs correspond to detaching a \( \sigma \) electron from the HOMO-1 (\( b_1 \)) which leads to the neutral triplet (3B1) and singlet (1B1) final state, respectively, with the second and third VDE = 4.999 and 5.073 eV at CCSD(T)//B3LYP and VDE = 4.896 eV and 4.969 eV at CCSD(T)//MP2. These VDE values define an approximate term value of \( T_1 = 1.22 \) eV for the first excited state (3B1) of C6O6. As shown in Table 2 (U)OVGF calculations also produce VDE values well in agreement with the more accurate CCSD(T) method for C6O6.

4. Summary

We have performed comprehensive first-principles calculations on the geometrical and electronic structures of C5O5 and C6O6.
oxocarbons in this work to complete CCSD(T) calculations on the whole monocyclic CnO3n/0 series (n = 3–6) [28,31–33]. The ground state of C6O6 anion favors perfect planar D3h symmetry, while C5O5 anion possesses a quasi-planar Cs symmetry. The electron affinities of C5O5 and C6O6 calculated at CCSD(T) appear to be about 0.2–0.3 eV higher than the corresponding value (3.475 eV) of C4O4 [19]. The term values of the first excited states of C5O5 and C6O6 neutrals are predicted to be much higher than the corresponding value of C4O4 [19]. The symmetrical ring breathing frequencies of C5O5 and C6O6 are predicted to be around 1750 cm⁻¹, slightly lower than that of smaller-sized C4O4 [19].

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