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Search for Ionic Orthocarbonates: Ab Initio Study of Na_4CO_4

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Ab initio calculations on a variety of structures have been performed for the Na_4CO_4 stoichiometry to test stability of the orthocarbonate structure. We found that the orthocarbonate structure is a true minimum on the potential energy surface, but it is not the most stable one. The most stable structure can be characterized as a complex of sodium carbonate and sodium oxide. However, the orthocarbonate structure was found to be just 13.8 kcal/mol higher in energy at our highest level of theory (CCSD(T)/6-311+G(2df)), and it is separated from the global minimum structure by the 9.2 kcal/mol barrier (B3LYP/6-311+G*) and 13.9 kcal/mol (CCSDCT)/6-311+G(2df)//B3LYP/6-311+G*). We hope that by selecting appropriate countercations the orthocarbonate structure can be further stabilized and may even become the most stable one. We also believe that in the solid state under high-pressure conditions there is a chance to convert the carbonate structure into the orthocarbonate structure because of its smaller volume.

I. Introduction

Carbonates and orthocarbonates represent a bizarre story in chemistry. Carbonic acid is a diprotic acid and can be considered to be formed by the hydration of carbon dioxide. This process is one of the most fundamental reactions in biological systems.[1,2] The acidic nature of carbonated water is also partly responsible for the long shelf life of many soft drinks and beer. Yet, H_2CO_3 is a surprisingly elusive compound, and in solution, CO_2 is only partly in the form of H_2CO_3 but is largely present as the more loosely hydrated species CO_2(aq).[3] Despite difficulties in the experimental characterization of H_2CO_3, it has been well studied by ab initio calculations.[4−8] It was found that the isolated H_2CO_3 is not a thermodynamically stable molecule but that it is a kinetically stable species because of a high dissociation barrier, which opens the possibility to detect H_2CO_3 in outer space. However, the presence of water substantially reduces the barrier for the H_2CO_3 dissociation and makes carbonic acid in aqueous solution decompose quickly.[8] Despite the elusive nature of carbonic acid, ionic carbonates are among the most abundant chemicals on Earth, viz., calcite, $CaCO_3$, magnesite, $MgCO_3$, dolomite, $MgCa(CO_3)_2$, etcetera. Calcite is the principal mineral in limestone rock, marble, chalk, coral reefs, and the shells of marine animals.

Orthocarbonic acid is a tetraprotic acid and can be considered to be formed by the double hydration of carbon dioxide, yet it has not been observed. However, it was shown computationally[9,10] that H_4CO_4 is a local minimum with the most stable structure adopting S_4 symmetry. We are not aware of any known ionic orthocarbonate salts; even ionic orthosilicates are dominant silicon-containing minerals. Despite the absence of orthocarbonic acid and its ionic salts, the orthocarbonate $(RO)_4C$ and $(ArO)_4C$ esters are well-known.[10] The acid-catalyzed hydrolysis of $(EtO)_4C$ played an important role in the formation of the Bronsted catalysis law.[11] In this article, we provide an ab initio exploration of the ionic orthocarbonate structure of Na_4CO_4 in order to explain why ionic orthocarbonate species have not been observed and under what conditions their existence is possible.

II. Computational Methods

We first optimized geometries and calculated harmonic frequencies of various Na_4CO_4 structures employing analytical gradients with polarized split-valence basis sets (6-311+G*)[12−14] with a hybrid method that includes a mixture of Hartree−Fock exchange with density functional exchange correlation functionals (B3LYP).[15−17] The lowest-energy structures identified were refined at the second order of the Moller−Plesset perturbation theory MP2.[18] Finally, the energies of the most stable structures were refined even further using the coupled-cluster theory[19−21] including single and double excitations and triple excitations evaluated perturbationally (CCSD(T)) and with 6-311+G(2df) basis sets. The core electrons were frozen while treating the electron correlation at the MP2 and CCSD(T) levels of theory. All calculations were performed using the Gaussian 98 program.[22]

III. Computational Results

First, we optimized the geometry of the orthocarbonate Na_4CO_4 structure with four sodium atoms coordinated to a face of the tetrahedral structure of the CO_4^{4-} tetraanion (Figure 1a). We found that this structure is a true minimum at both the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. Calculated harmonic frequencies are in good agreement at two levels of theory (Table 1) and can be used to identify this structure, which was found to be thermodynamically stable toward the two lowest monomolecular dissociation channels:

$$Na_4CO_4\ (T_d,\ {}^1A_1) \rightarrow Na_4O_2\ (D_{2h},\ {}^1A_g) + CO_2 \qquad +72.2\ \text{kcal/mol} \quad (1)$$

$$Na_4CO_4\ (T_d,\ {}^1A_1) \rightarrow Na_2CO_3\ (C_{2v},\ {}^1A_1) + Na_2O \qquad +50.2\ \text{kcal/mol} \quad (2)$$

(all at CCSD(T)/6-311+G(2df)//MP2/6-311+G*). These data shows that the ionic orthocarbonate Na_4CO_4 structure is viable. The natural population analysis (NPA) performed at the MP2/6-311+G* level of theory shows that the chemical bonding inside the CO_4^{4-} tetraanion is rather covalent, but it is purely

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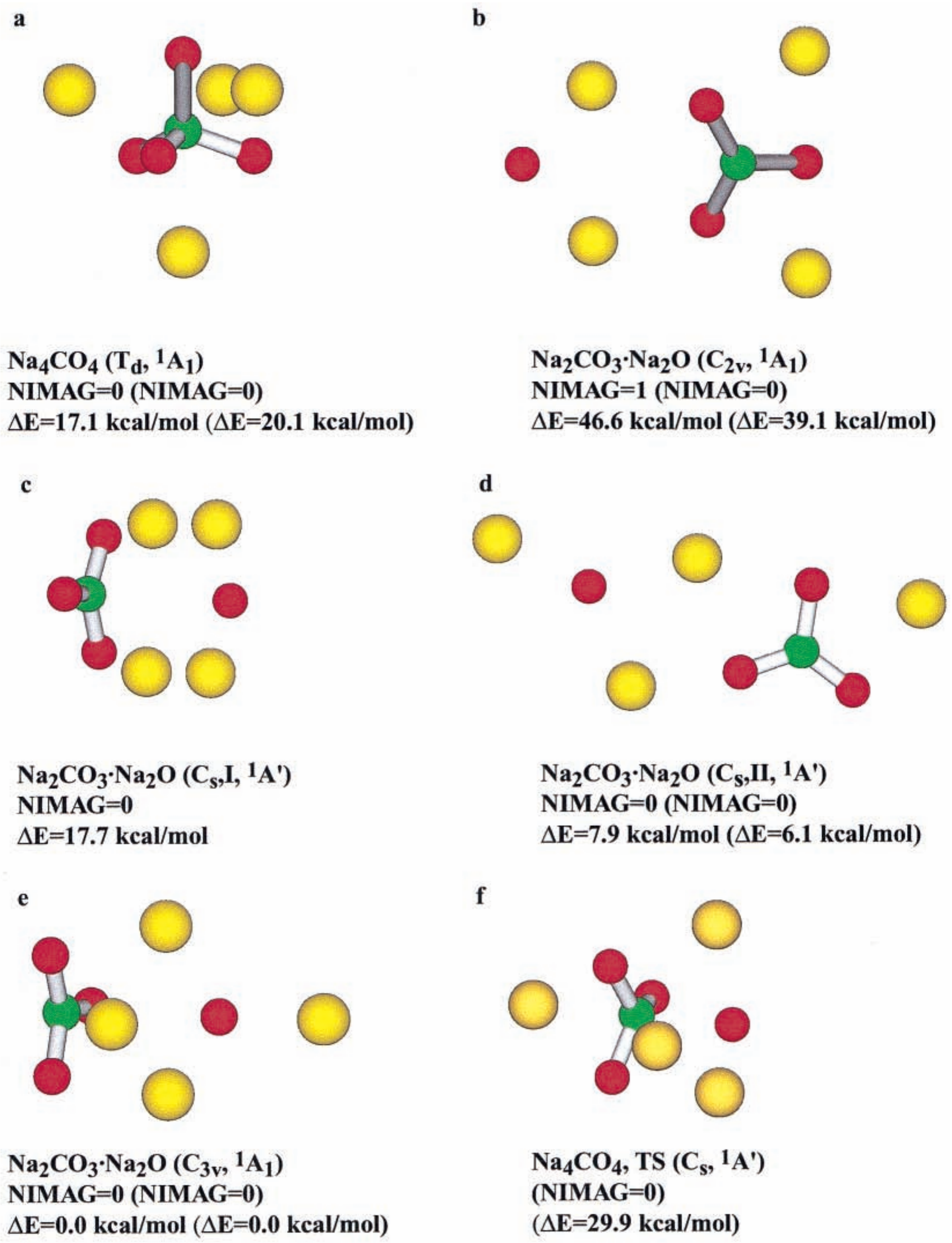

Figure 1. Optimized structures of (a) Na_4CO_4 (T_d, $^1A_1$), (b) Na_4CO_4 (C_{2v}, $^1A_1$), (c) Na_4CO_4 (C_s, I, $^1A'$), (d) Na_4CO_4 (C_s, II, $^1A'$), (e) Na_4CO_4 (C_{3v}, $^1A_1$), and (f) Na_4CO_4 TS (C_s, $^1A'$) at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. Data at the B3LYP/6-311+G* level of theory are given in parentheses.

ionic between Na^+ cations and the tetraanion. The representative NPA effective charges are the following (AO populations are given in parentheses): $Q(C) = +0.83e$ ($2s^{0.77}2p^{2.24}$); $Q(O) = -1.14e$ ($2s^{1.78}2p^{5.28}$); $Q(Na) = +0.93e$ ($3s^{0.05}2p^{0.01}$). An isolated CO_4^{4-} anion is certainly highly unstable because of the high Coulomb repulsion between four extra charges, but four countercations stabilize the tetraanion in the orthocarbonate structure. However, when just one countercation is detached, the resulting orthocarbonate $Na_3CO_4^-$ structure is not a minimum anymore. Therefore, we must strike quite a delicate balance between the stabilizing and destabilizing forces in the Na_4CO_4 orthocarbonate.

We also test many alternative structures that can be viewed as complexes of Na_2CO_3 and Na_2O without the formation of the CO_4^{4-} tetraanion. The structures that are a local minimum for at least one level of theory are shown in Figure 1. The planar $Na_2CO_3{\cdot}Na_2O$ structure (C_{2v}, $^1A_1$, Figure 1b) was found to be a local minimum at the B3LYP/6-311+G* level of theory, and it is 19.0 kcal/mol higher in energy than the T_d structure. However at the MP2/6-311+G* level of theory, it is a first-order saddle point. Geometry optimization following the imaginary frequency mode leads to the out-of-plane distortion and to the structure (C_s, I, $^1A'$) (Figure 1c) that is now a local minimum. The (C_s, I, $^1A'$) structure was found to be less stable than the orthocarbonate structure by 3.6 kcal/mol (CCSD(T)/6-311+G(2df).

While searching for the global minimum structure, we found another $Na_2CO_3{\cdot}Na_2O$ complex structure of C_s symmetry (C_s,

TABLE 1: Calculated Molecular Properties of the Orthocarbonate Na_4CO_4 (T_d, $^1A_1$) Isomer[a]

B3LYP/6-311+G*	MP2/6-311+G*
$E_t = -988.506525$ au	$E_t = -985.971390$ au[b]
$R(C-O) = 1.430$ Å	$R(C-O) = 1.431$ Å
$R(C-Na) = 2.288$ Å	$R(C-Na) = 2.328$ Å
$R(Na-O) = 2.258$ Å	$R(Na-O) = 2.290$ Å
$\omega_1(a_1) = 811$ (0.0) cm^{-1}	$\omega_1(a_1) = 818$ (0.0) cm^{-1}
$\omega_2(a_1) = 329$ (0.0) cm^{-1}	$\omega_2(a_1) = 333$ (0.0) cm^{-1}
$\omega_3(e) = 527$ (0.0) cm^{-1}	$\omega_3(e) = 528$ (0.0) cm^{-1}
$\omega_4(e) = 134$ (0.0) cm^{-1}	$\omega_4(e) = 136$ (0.0) cm^{-1}
$\omega_5(t_1) = 255$ (0.0) cm^{-1}	$\omega_5(t_1) = 258$ (0.0) cm^{-1}
$\omega_6(t_2) = 970$ (332) cm^{-1}	$\omega_6(t_2) = 985$ (397) cm^{-1}
$\omega_7(t_2) = 632$ (25) cm^{-1}	$\omega_7(t_2) = 639$ (21) cm^{-1}
$\omega_8(t_2) = 379$ (186) cm^{-1}	$\omega_8(t_2) = 382$ (216) cm^{-1}
$\omega_8(t_2) = 156$ (27) cm^{-1}	$\omega_8(t_2) = 159$ (31) cm^{-1}

[a] IR intensities (in km/mol) are given in parentheses. [b] $E_t = -986.198244$ au at the CCSD(T)/6-311+G(2df) level of theory using the MP2/6-311+G* geometry.

TABLE 2: Calculated Molecular Properties of the Most Stable Na_4CO_4 (C_{3v}, $^1A_1$) Isomer[a]

B3LYP/6-311+G*	MP2/6-311+G*
$E_t = -988.538506$ a. u.	$E_t = -985.998565$ au[b]
$R(C-O_t) = 1.298$ Å	$R(C-O_t) = 1.304$ Å
$R(C-O_b) = 3.127$ Å	$R(C-O_b) = 3.149$ Å
$R(O_b-Na_t) = 2.033$ Å	$R(O_b-Na_t) = 2.077$ Å
$R(C-Na_b) = 2.468$ Å	$R(C-Na_b) = 2.509$ Å
$<O_bCO_t = 86.8°$	$<O_bCO_t = 87.3°$
$<O_bCNa_b = 45.7°$	$<O_bCNa_b = 46.2°$
$\omega_1(a_1) = 1038$ (1) cm^{-1}	$\omega_1(a_1) = 1051$ (5) cm^{-1}
$\omega_2(a_1) = 895$ (30) cm^{-1}	$\omega_2(a_1) = 898$ (38) cm^{-1}
$\omega_3(a_1) = 565$ (120) cm^{-1}	$\omega_3(a_1) = 532$ (109) cm^{-1}
$\omega_4(a_1) = 347$ (96) cm^{-1}	$\omega_4(a_1) = 364$ (139) cm^{-1}
$\omega_5(a_1) = 254$ (34) cm^{-1}	$\omega_5(a_1) = 237$ (35) cm^{-1}
$\omega_6(a_1) = 170$ (11) cm^{-1}	$\omega_6(a_1) = 159$ (12) cm^{-1}
$\omega_7(a_2) = 207$ (0) cm^{-1}	$\omega_7(a_2) = 205$ (0) cm^{-1}
$\omega_8(e) = 1401$ (551) cm^{-1}	$\omega_8(e) = 1445$ (578) cm^{-1}
$\omega_9(e) = 686$ (1) cm^{-1}	$\omega_9(e) = 689$ (2) cm^{-1}
$\omega_{10}(e) = 316$ (121) cm^{-1}	$\omega_{10}(e) = 325$ (140) cm^{-1}
$\omega_{11}(e) = 264$ (8) cm^{-1}	$\omega_{11}(e) = 256$ (15) cm^{-1}
$\omega_{12}(e) = 239$ (21) cm^{-1}	$\omega_{12}(e) = 236$ (22) cm^{-1}
$\omega_{13}(e) = 177$ (6) cm^{-1}	$\omega_{13}(e) = 167$ (5) cm^{-1}
$\omega_{14}(e) = 78$ (2) cm^{-1}	$\omega_{14}(e) = 77$ (2) cm^{-1}

[a] IR intensities (in km/mol) are given in parentheses. [b] $E_t = -986.220259$ au at the CCSD(T)/6-311+G(2df) level of theory using the MP2/6-311+G* geometry.

II, $^1A'$), which shown in Figure 1d. The planar (C_s, II, $^1A'$) structure was found to be more stable than the orthocarbonate structure by 5.7 kcal/mol (CCSD(T)/6-311+G(2df).

However, from our search for the most stable structure, we found that a (C_{3v}, $^1A_1$, Figure 1e) $Na_2CO_3 \cdot Na_2O$ complex is a global minimum. It is more stable than the orthocarbonate structure by 13.8 kcal/mol (CCSD(T)/6-311+G(2df)). This number is not very large, and that opens the possibility of finding appropriate cations that can increase the relative stability of the orthocarbonate structure.

We also performed a search of the transition state on the intramolecular rearrangement of the orthocarbonate structure T_d ($^1A_1$) to the global minimum structure C_{3v} ($^1A_1$). The height of the barrier (structure TS, Figure 1f) was calculated to be 9.2 kcal/mol (ZPE-corrected) at the B3LYP/6-311+G* level of theory and 13.9 kcal/mol at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G* level of theory. We therefore believe that if the othrocarbonate isomer is made in the matrix isolation it will survive.

IV. Discussion

We found in our calculations that the orthocarbonate Na_4CO_4 (T_d, $^1A_1$) structure with a $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^4 3t_2^6 1t_1^6 3a_1^0$ electronic configuration is a true minimum, but it is not the most stable structure for that stoichiometry. It was found to be 13.8 kcal/mol higher in energy than the most stable $Na_2CO_3 \cdot Na_2O$ structure (C_{3v}, $^1A_1$) (Table 2). The lower stability of the orthocarbonate structure comes primarily from a high extra charge (−4) on the rather small penta-atomic CO_4 group. When one cation is removed in the $Na_3CO_4^-$ anion, the orthocarbonate structure is not a minimum anymore. Therefore, we need to have four cations around the CO_4^{4-} tetraanion to keep it stable. One way to stabilize the tetraanion even more is to choose appropriate countercations with more covalent contributions to the bonding, which can enhance its stability. It should be remembered that the covalently bound $(RO)_4C$ esters are well-known to be stable. There is another way to increase the relative stability of the ionic orthocarbonates. The orthocarbonate structures are substantially more compact than the alternative structures. From our calculations, we evaluated the electronic spatial extent ($\langle R^2 \rangle$) for both the Na_4CO_4 and $Na_2CO_3 \cdot Na_2O$ structures. $\langle R^2 \rangle$ is a characteristic of the size of the system. According to our calculations, the most stable carbonate (C_{3v}, $^1A_1$) structure is 26% larger than the orthocarbonate Na_4CO_4 structure. It is well-known that under high-temperature conditions ionic carbonates release CO_2, leaving ionic oxide. However, on the basis of our results, we hope that in the solid state under high-pressure conditions there is a chance to stop the decomposition of an ionic carbonate at 50% of the CO_2 release and thus convert the carbonate structure into the orthocarbonate. The orthocabonates probably can survive as metastable solids even when high pressure is removed. It would be interesting to discover if species such as $MgCO_3 \cdot MgO$ or $CaCO_3 \cdot CaO$ can be transformed into orthocarbonate magnesium Mg_2CO_4 or calcium Ca_2CO_4 under high pressure. Such transformations may be important in better understanding the properties of carbonates in the inner layers of Earth. We hope that our results will attract attention to the possibility of synthesizing ionic orthocarbonate solids.

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