Ab Initio Calculations on the Structure of Covington's Sesquicarbonate Ion

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Ab initio calculations suggest that the sesquicarbonate ion, $H_3C_2O_6^-$, may well exist but has a planar structure (**6**) held together by two hydrogen bonds instead of the 'sandwich' structure (**1**) or (**2**) proposed by Covington; the planar structures lies 182 kJ mol^{-1} below the sum of the energies of bicarbonate ion and (*Z,Z*)-carbonic acid.

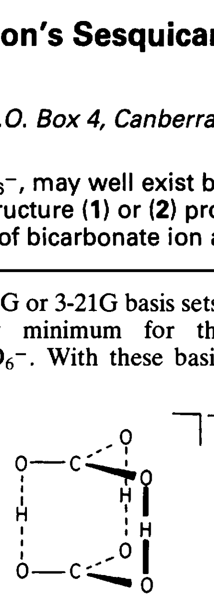
Covington has suggested[1] that, to explain his potentiometric-titration results, there may exist a sesquicarbonate ion, $H_3C_2O_6^-$, for which he proposed a 'sandwich' structure (**1**) described as 'two planar carbonate moieties linked by bridging hydrogen bonds to oxygen atoms.'

Beginning with a D_{3h} structure of this ilk but in which each hydrogen atom was permitted to determine independently the optimum distances from its two associated oxygen atoms, one in each CO_3 plane, optimization with the STO-3G basis set[2] led first to a C_{3v}, and finally to a C_1 (near C_s) structure (**2**); this lay, however, 5.0 kJ mol^{-1} above the sum of the energies of its components, bicarbonate ion (**3**) and (*E,E*)-carbonic acid (**4**), the latter of which itself lies 40.6 kJ mol^{-1} above the (*Z,Z*)-form (**5**).

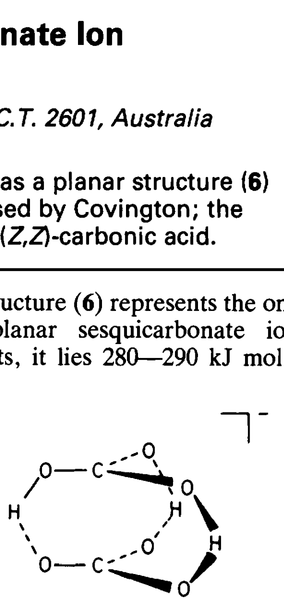
Reoptimization with the STO-3G and 3-21G[3] basis sets from this parallel arrangement of the two CO_3 groups but under conditions that permitted the two CO_3 groups to become non-parallel and each CO_3 group to become non-planar led to a progressively greater distance between the two carbon atoms and a corresponding increase in the angle between the (still near-planar) CO_3 groups. It was clear that, at these levels of theory, the sandwich-type structure suggested[1] by Covington does not represent a stable equilibrium species.

Optimization from this point was continued under conditions that permitted the unique (non-hydrogen-bonded) proton to adopt any preferred position in or out of the adjacent CO_3 plane. With either basis set, the optimized structure was fully coplanar and, on the basis of lengths of the CO and OH bonds, best described as structure (**6**).†

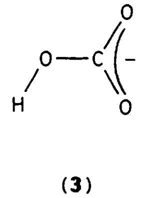
It was then of interest to determine whether structures such as (**7**), (**8**), or (**9**) may also represent equilibrium structures and, if so, what are their relative energies. Reoptimization beginning near structure (**9**), has shown that, with either STO-3G or 3-21G basis sets, structure (**6**) represents the only energy minimum for the planar sesquicarbonate ion, $H_3C_2O_6^-$. With these basis sets, it lies 280—290 kJ mol^{-1}



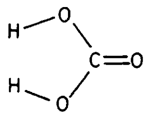
(**1**)



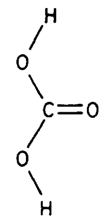
(**2**)



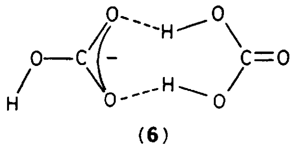
(**3**)



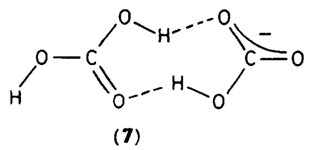
(**4**)



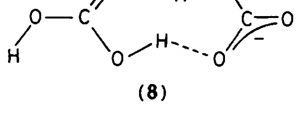
(**5**)



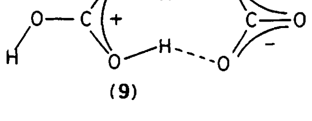
(**6**)



(**7**)



(**8**)



(**9**)

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† C=O lengths are <1.23 Å, whereas C–O lengths are >1.33 Å; O–H lengths are <1.1 Å, whereas O --- H distances are >1.4 Å.

below the sum of the energies of its constituents, bicarbonate ion (**3**) and (*E*,*E*)-carbonic acid (**4**) [230—240 kJ mol^{-1}, if the lower-energy (*Z*,*Z*)-structure (**5**) is used as reference instead of (**4**)]. For comparison the cyclic dimer of methanoic acid lies 63(STO-3G)—112(3-21G) kJ mol^{-1} below twice the energy of the monomer, (*Z*)-methanoic acid.

It is, however, known[4] that diffuse functions, although having little effect on optimized geometries, must be included for accurate evaluation of relative energies of anionic species. We have therefore evaluated the energies of the 3-21G-optimized structures, (**3**), (**4**), (**5**), and (**6**), with the 3-21+G basis set,[4] and find that, at this improved level, structure (**6**) lies 182.3 kJ mol^{-1} below the sum of the energies of structures (**3**) and (**5**). In principle, we should also take account of the basis-set superposition error;[5] here, however, because of the large distances between first-row atoms in the left- (**3**) and right-hand (**4**) constituent fragments of structure (**6**), this error will lower the above-calculated energy difference only marginally.

It therefore appears that the sesquicarbonate ion, $H_3C_2O_6^-$, may well exist as the planar structure (**6**), thermodynamically stable with respect to its components, bicarbonate ion (**3**) and carbonic acid, (**4**) or (**5**). This result, of course, takes no account of other thermodynamics or of dynamics in the carbon dioxide–water system.

The above calculations were made with a locally-modified[6] version of the Gaussian 82 series of programs.[7] Detailed results, including those for methanoic acid and its dimer, will be published elsewhere.

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