

Has the Dimer of Carbonic Acid a Lower Energy Than Its Constituents Water and Carbon Dioxide?

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Received May 29, 1996. Revised Manuscript Received January 6, 1997[⊗]

Abstract: On the basis of high-level molecular quantum mechanics, the zero-point-corrected energy for formation of the anti-anti conformer of carbonic acid from water and carbon dioxide is compensated by formation of the most stable dimer. Therefore, the zero-point-corrected energy for formation of the carbonic acid dimer from its constituents water and carbon dioxide is close to zero, and even slightly negative values seem to be possible. These results include new CCSD(T)/6-311++G(3df,3pd) calculations of the formation energy of carbonic acid from water and carbon dioxide, which gave an energy difference of between 8.2 and 9.2 kcal/mol which is lower than those reported before. Furthermore, the dimerization energy of carbonic acid and formic acid is reported up to the MP2/aug-cc-pVTZ level of theory, leading to a best estimate of -16.9 kcal/mol for the carbonic acid dimer relying on convergence considerations for the MP2/aug-cc-pVxZ level of theory that also clearly reveal the failure of counterpoise correction for basis set superposition error. We conclude that in our atmosphere formation of a dimer of carbonic acid is disfavored mainly by entropy, and not by enthalpy.

1. Introduction

Recent experimental investigations have shown that carbonic acid has to be considered a real existing species^{1–8} under conditions that kinetically hinder its decomposition. However, high-level theoretical investigations predict the carbonic acid monomer to be thermodynamically unstable with respect to decomposition into water and carbon dioxide.⁹ Nevertheless, the typical structural arrangement of carboxylic acids in the gaseous and crystalline states is not a monomer-dominated one but rather a very stable dimer.^{10–12} These dimer structures gain their extraordinary stability from a planar six-membered ring structure formed by the hydrogen bonds between the two carboxyl groups in the dimer. Therefore, the carbonic acid dimer is more relevant for investigating the stability of carbonic acid than the monomer. We show here by high-level molecular quantum mechanical calculations that the zero-point-corrected energy for formation of the most stable dimer of carbonic acid

from its constituents water and carbon dioxide is close to 0, and even slightly negative values seem possible. We conclude that in our atmosphere formation of a dimer of carbonic acid is disfavored mainly by entropy and not by enthalpy.

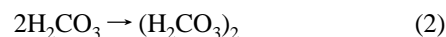
2. Methods and Calculations

The formation of the carbonic acid dimer from water and carbon dioxide consists of two rather different steps. The first step is the formation of carbonic acid monomer from water and carbon dioxide which is electronically complicated due to the breaking and forming of covalent bonds.



This step is well-documented in the literature.^{4,9,13–15} However, we will show below that a highly accurate description of this step is crucial for all further conclusions.

The second step is the formation of the hydrogen-bonded complex from two monomers.



Fortunately, the proper quantum mechanical description of this second step that includes twice the number of atoms is comparably less demanding. Therefore, we attempted to obtain theoretically “converging” results for these two reactions both for the energetics and for the zero-point energy separately. All calculations were done with the Gaussian94¹⁶ and ACES II¹⁷ packages of programs.

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⊗ Abstract published in *Advance ACS Abstracts*, February 1, 1997.

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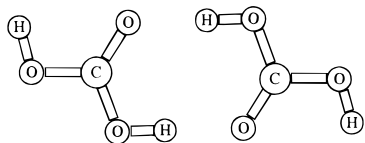


Figure 1. Carbonic acid dimer structure.

Table 1^a

method	ΔE	ΔZPE
B3LYP/6-31+G(p)	1.14	4.22
B3LYP/aug-cc-pVDZ	3.05	4.20
B3LYP/6-311++G(3df,3pd)	4.79	4.14
B3LYP/aug-cc-pVTZ	4.79	
MP2/6-31+G(p)	5.48	4.23
MP2/cc-pVDZ	4.55	
MP2/aug-cc-pVDZ	7.06	4.26
MP2/cc-pVTZ	4.38	
MP2/6-311++G(3df,3pd)	6.25	
MP2/aug-cc-pVTZ	5.45	
MP2/cc-pVQZ	5.06	
CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ	3.53	
CCSD(T)(full)/aug-cc-pVDZ//MP2/aug-cc-pVDZ	4.01	
CCSD(T)/6-311++G(3df,3pd)//MP2/aug-cc-pVDZ	4.33	
CCSD(T)(full)/aug-cc-pVDZ	4.60	

^a ΔE is the energy difference, and ΔZPE is the zero-point energy difference of the reaction $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$ [kcal/mol] (due to fast convergence and high computational demands, ΔZPE values were only calculated for some selected levels of theory).

2.1. Formation of Carbonic Acid. As already pointed out by others,^{9,18} the most stable conformation of carbonic acid involves an anti-anti orientation of the two hydrogens (i.e., both hydrogens point toward the carbonyl oxygen). Throughout this study, we exclusively concentrated on this anti-anti orientation of carbonic acid both for the monomer and the dimer (as shown in Figure 1).

Estimates at HF/3-21G level¹⁵ predicted the carbonic acid to be -12.6 kcal/mol more stable than water and carbon dioxide even though in 1976 Jönsson et al.^{13,14} emphasized the importance of electron correlation. It was shown recently⁴ that larger basis sets and inclusion of electron correlation result in the opposite picture. The highest level calculations published so far⁹ at the QCISD(T)/6-311++G** level disfavor carbonic acid by 10.4 kcal/mol (zero-point-corrected energy) with respect to water and carbon dioxide. The authors⁹ gave an error estimate of less than 2.4 kcal/mol for their result.

Our calculations, summarized in Table 1, demonstrate that the zero-point energy correction (ΔZPE) converges very fast on increasing the level of theory and that it is only a very minor source of errors. However, the situation for the energy difference (ΔE) is completely different and much more complicated. ΔE varies by as much as 3.5 kcal/mol between MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ calculations, both frozen core and at the MP2/aug-cc-pVDZ geometries. On assuming a ΔZPE value of about 4.2 kcal/mol, the MP2/6-311++G(3df,3pd) result agrees quite well with the value published by White and Boldyrev.⁹ In comparison to the 6-311++G(3df,3pd) basis sets of Pople and co-workers,^{19–21} the augmented correlation consistent basis sets of Dunning and co-workers^{22–24} give slightly lower energy differences, whereas the correlation consistent basis sets without augmented diffuse functions tend to be substantially lower.

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Table 2. Energetics of $2\text{H}_2\text{CO}_3 \rightarrow (\text{H}_2\text{CO}_3)_2$ [kcal/mol]

method	ΔE	ΔZPE
B3LYP/6-31+G(p)	-18.02	1.47
B3LYP/aug-cc-pVDZ	-17.76	1.23
MP2/6-31+G(p)	-18.32	1.74
MP2/aug-cc-pVDZ	-18.50	1.43
MP2/aug-cc-pVTZ	-18.96	

However, on both increasing the level of theory and enlarging the basis sets, “convergence” toward a ΔE of between 4.0 and 5.0 kcal/mol is observable (Table 1). To ensure that the lowering of ΔE is not a result of deficiencies in our single-determinant approaches concerning nondynamic electron correlation, we calculated the T1 diagnostics^{25,26} for the involved species at the CCSD(T)/6-311++G(3df,3pd)/MP2/aug-cc-pVDZ level. As can be expected, water is very well-described in its equilibrium geometry by one-determinant approaches, reflected by a T1 diagnostic of 0.010. The T1 diagnostics of 0.019 for carbon dioxide and 0.015 for carbonic acid seem to imply that most of the problems describing the correct ΔE emerge from the proper description of electron correlation in carbon dioxide. CCSD(T) should be able to handle electron correlation of systems with T1 diagnostics around 0.02 rather well.²⁵ Therefore, we consider our CCSD(T)/6-311++G(3df,3pd)/MP2/aug-cc-pVDZ and CCSD(T)(full)/aug-cc-pVDZ calculations resulting in an energy difference of 4.33 and 4.60 kcal/mol, respectively, as results approaching “chemical accuracy” of 1.0 kcal/mol. Consequently, by using 4.0–5.0 kcal/mol for ΔE and 4.2 kcal/mol for ΔZPE , we obtain a zero-point-corrected energy for formation of carbonic acid from water and carbon dioxide between ~ 8.2 and 9.2 kcal/mol which is lower than the previous high-level calculations by 1–2 kcal/mol.⁹

2.2. Formation of Carbonic Acid Dimer. Extensive investigations on possible dimer configurations have shown²⁷ that the most stable configuration is built up by two anti-anti monomers, as displayed in Figure 1. ΔE and ΔZPE for the dimer complex formation are given in Table 2.

As mentioned above, we consider the proper description of the two additional hydrogen bonds in reaction 2 (eq 2) as theoretically much less demanding than reaction 1 (eq 1). To estimate the effects of the so-called basis set superposition error,²⁸ the improvement of the monomers description by the basis functions of the other monomer in the dimer geometry were calculated. They amount to -0.36 kcal/mol for B3LYP/aug-cc-pVDZ, -1.45 kcal/mol for MP2/aug-cc-pVDZ, and -0.91 kcal/mol for MP2/aug-cc-pVTZ level of theory and would result in a counterpoise-corrected ΔE of -17.04 , -15.60 , and -17.13 kcal/mol, respectively. However, recent high-level benchmark studies on the dimers of hydrogen fluoride^{29,30} and water³¹ impressively show that counterpoise correction deteriorates the convergence of hydrogen bond description at MP2/aug-cc-pVxZ level dramatically, whereas non-counterpoise-corrected energies are excellently close to the best estimate throughout the whole MP2/aug-cc-pVxZ series starting from the MP2/aug-cc-pVDZ level of theory. Comparable high-level calculations for the carbonic acid dimer—being a 64 electron system—are not feasible yet.

To still take advantage of the knowledge gathered about the convergence behavior of MP2/aug-cc-pVxZ description of hydrogen bonds, we scaled ΔE with and without counterpoise correction to the best estimates^{29–31} for ΔE for the dimer of water and hydrogen fluoride, as shown in Figure 2. Assuming a very similar basis set convergence behavior for the carbonic acid dimer, we found -18.3 kcal/mol as the best estimate for ΔE . To verify this assumption of very similar basis set convergence behavior, we applied the same procedure to the dimer of formic acid (ΔE rises to -16.42 kcal/mol without and to -13.92

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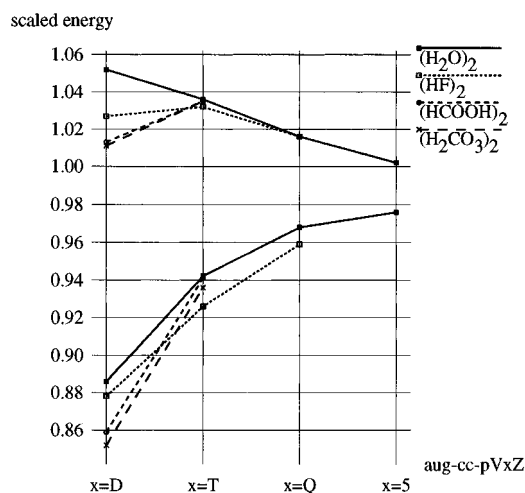


Figure 2. ΔE (upper line) and counterpoise-corrected ΔE (lower line) for the dimer of water,³¹ hydrogen fluoride,²⁹ formic acid, and carbonic acid at MP2/aug-cc-VxZ level of theory scaled to the best estimate for the dimerization energy (-5.0 kcal/mol for $(\text{H}_2\text{O})_2$, -4.56 kcal/mol for $(\text{HF})_2$, -16.2 kcal/mol for $(\text{HCOOH})_2$, and -18.3 kcal/mol for $(\text{H}_2\text{CO}_3)_2$).

kcal/mol with counterpoise correction at the MP2/aug-cc-pVDZ level and to -16.78 kcal/mol without and -15.24 kcal/mol with counterpoise correction at the MP2/aug-cc-pVTZ level of theory). The resulting best estimate for the dimerization energy of formic acid of -16.2 kcal/mol is in excellent agreement with the $G2^*$ result (-16.15 kcal/mol) recently published by Kim.³²

It is quite obvious that the counterpoise-corrected dimerization energy at the MP2/aug-cc-pVDZ level strongly underestimates the dimerization energy both for the carbonic acid dimer as well as for the formic acid dimer, as is the case for the very well-studied 20 electron systems, hydrogen fluoride and water dimer. Schwenke and Truhlar showed

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more than a decade ago^{33–35} that the counterpoise correction does not systematically improve the accuracy of the calculation of the interaction energy of two hydrogen fluoride molecules at Hartree–Fock level of theory. Also, at the MP2/aug-cc-pVxZ level of theory it is obvious that counterpoise correction is very counterproductive for the proper description of hydrogen bonds and even considerably deteriorates the convergence behavior of the calculated interaction energies.

Finally, on considering that the errors introduced in the calculation of the monomer formation double on estimating the dimer formation energy from water and carbon dioxide, the range between the MP2/aug-cc-pVTZ value of -18.96 kcal/mol and our best estimate of -18.3 kcal/mol for ΔE of the two monomers and the dimer (resulting in a zero-point-corrected energy of about -17.5 and -16.9 kcal/mol, respectively) is of an accuracy comparable to our highest level calculations for the formation of the monomer. Details on the dimer calculations including frequency shifts and discussion of finite temperature thermodynamics will be given elsewhere.²⁷

3. Conclusions

Combining the value of about 8.2 – 9.2 kcal/mol for the zero-point-corrected energy of the monomer with respect to water and carbon dioxide with the zero-point-corrected energy of about -16.9 to -17.5 kcal/mol for the dimer formation leads to nearly perfect compensation. It is not possible to judge from the present calculations if the zero-point-corrected energy for the formation of the carbonic acid dimer from water and carbon dioxide is slightly positive or slightly negative; however, it is astonishingly close to 0.

Acknowledgment. We are grateful for financial support by the National Bank of Austria (project no. 5235) and the Forschungsförderungsfonds of Austria (project no. P10404-PHY).

JA961802Q

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