versations. They also wish to thank Professor Kenneth B. Wiberg for copies of manuscripts prior to publication. Financial support from the National Institutes of Health, No. GM26462, is gratefully acknowledged. One of us (J.E.J.) thanks the National Science Foundation for support through Grant CHE 8101212 to Maitland Jones, Jr.

Note Added in Proof. (a) Bader[26] has applied his topological theory of molecular structure to the interpretation of the charge distribution along the C_1–C_3 axis in [1.1.1]propellane (computed with the 4-31G basis). He finds a long and weak C_1–C_3 bond in the equilibrium structure which upon elongation passes through an unstable coalescence of critical points to a cage structure of three inwardly curved four-membered rings. In agreement with Newton and Schulman,[7] we interpret our 6-31G* charge density along C_1–C_3 as antibonding at equilibrium separation.

(b) Epiotis has employed his bond-diagrammatic molecular orbital valence bond theory[27,28] to qualitatively discuss bond-deficient molecules and [1.1.1]propellane in particular.[28,29] In the latter reference,[29] he has set up an in principle computable ratio, λ_U/λ_D, that predicts whether or not a molecule has one less bond than expected from Lewis dot structures, and he has given several examples in addition to propellane.

(c) Deformation densities from a recent X-ray study[30] of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one show nothing extraordinary about the central bond in this species. Thus, the unusual deformation density reported for III specifically characterized bonding between inverted bridgehead atoms and is not simply peculiar to molecules containing the bicyclobutane skeleton.

Registry No. [1.1.1]Propellane, 35634-10-7; 1,3-diborabicyclo-[1.1.1]pentane, 87902-15-6; bicyclo[1.1.1]pentane, 311-75-1; 1,3-diazabicyclo[1.1.1]pentane, 71634-25-8; bicyclo[1.1.1]pentyl-1-carbenium ion, 22907-79-5.

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A Theoretical Study of the Formation of Carbonic Acid from the Hydration of Carbon Dioxide: A Case of Active Solvent Catalysis

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Abstract: The activation energy of CO_2 toward hydration has been calculated as 15.5 kcal/mol by ab initio SCF calculations using the split-valence 3-21G basis set, which is in good agreement with the experimental value. A quite stable six-membered cyclic complex of CO_2 and the water dimer has been obtained by the calculation. The preferred hydration reaction is found to be that with the water dimer, the reaction with the water monomer being far less favored. The catalytic effect of the second water molecule in the hydration process has been discussed.

I. Introduction

The hydration of carbon dioxide, CO_2, is one of the more fundamental reactions in several biological and ecological process.[1] When CO_2 is dissolved at neutral pH, the dominant reactions are[2]

$$(CO_2)_{aq} + H_2O \overset{I}{\rightleftharpoons} (H_2CO_3)_{aq} \overset{II}{\rightleftharpoons} (HCO_3^-)_{aq} + (H^+)_{aq}$$

where the formation of carbonic acid (reaction I) is the rate-determining step, whereas the equilibrium (reaction II) with the bicarbonate ion is very fast. Even though carbonic acid has not yet been isolated or directly observed by any spectroscopic means, its existence has been inferred from kinetic evidence: the activation energy for the hydration of CO_2 in neutral solution is reported at 17.7 kcal/mol.[3]

From a theoretical point of view, several studies are available on the gas-phase reaction of the isolated entities:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

From their SCF calculations, Jönsson et al.[4,5] found an activation barrier for this reaction of 55.9 kcal/mol; the introduction of the electron correlation effect lowered the barrier only slightly to yield 52.3 kcal/mol. The very large discrepancy between theoretical and experimental values suggests that the reaction mechanism in solution might be fundamentally different from the mechanism in the gas phase.

In studying solvent effect, the solvent has perhaps too often been regarded as a continuous medium rather than as an active participant in the reaction. In what follows, we intend to show that the participation of a second water molecule in the reaction amounts to a significant catalytic effect. As a matter of fact, the idea of a second water molecule involvement was already advanced in Jönsson's original paper,[5] but it was not pursued any further at that time. Quite recently, however, the role of the water dimer

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[‡] Swiss Federal Institute of Technology.

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or water oligomers has been discussed in the study of a number of simple, or partly related, reactions.[6-9] In several cases, this led to a substantial lowering of the activation energy. Therefore, we dicided to carry out a detailed ab initio SCF comparison of the reactions

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$

and

$$CO_2 + 2H_2O \rightarrow H_2CO_3 + H_2O \qquad (2)$$

II. Optimization of the Relevant Structures

The geometry optimization has been carried out by means of the Hartree–Fock SCF method employing the split-valence 3-21G basis set[10] throughout. We have considered 12 stationary points on the relevant energy surfaces: H_2O, CO_2, $(H_2O)_2$, three $(CO_2–H_2O)$ complexes, one $(CO_2 + H_2O)$ transition state, three planar conformations of H_2CO_3, one $CO_2 + (H_2O)_2$ complex, and the transition state connecting the latter to $(H_2CO_3 + H_2O)$.

The molecular geometries for the stationary points have been optimized by the force method with use of the analytical gradient.[11] The optimally conditioned minimization technique[12] was employed for searching the minima or minimizing the energies. The geometry optimization was carried out for all geometrical parameters, except for the imposition of C_s symetry in the transition state.[13] The transition states were located by minimizing the gradient norm while ensuring that the matrix of the second derivatives of the energy had one negative eigenvalue. The Hessian matrices were computed by gradient differences with use of the VA05AD method.[14] It should be mentioned that the optimizations were terminated when the gradient length $g = (\sum_i^n(\delta E/\delta q_i)^2/n)^{1/2}$ was reduced below 5×10^{-4} mdyn. All calculation procedures are implemented in the MONSTERGAUSS program.[15]

The optimized geometrical parameters and the calculated SCF energies of the 12 stationary structures are shown in Figure 1. In agreement with the matrix-IR study[16] and previous ab initio work,[4] molecular complex **3** of Figure 1 turns out to be more stable than either **5** or even the hydrogen-bonded one (**4**).

The energies of formation were calculated at −7.9, −6.3, and −3.9 kcal/mol, respectively; these values are in good agreement with the results of Jönsson et al.,[4] who obtained −6.1, −4.9, and −2.9 kcal/mol with the double-ζ quality basis set. The geometry and the relative energies of the three planar conformations of carbonic acid **7**, **8**, and **9** may be compared with previous ab initio works by Jönsson et al.,[5] George et al.,[17] and Williams et al.[18] The calculated bond distances and bond angles are found to be in good agreement with the published results, except for the COH angle in **7**: our value of 111.8° is situated between 108.8° (Jönsson) and 112.6° (George). The trans-trans structure **7** is calculated to be the most stable conformation, although the cis-trans conformer **8** is only 1.0 kcal/mol higher in energy. The cis-cis structure **9** on the other hand is calculated at 13.8 kcal/mol above **7**. Although these values are quite comparable to previously reported results, there is one rather important difference: we find the cis-cis conformation **9** to be characterized by one negative eigenvalue of the second derivative matrix of the energy. Therefore, we conclude, in contrast to earlier studies,[17,18] that the cis-cis structure **9** corresponds to a saddle point rather than to a local minimum. The carbonic acid molecule, H_2CO_3, is thus characterized by two stable planar conformations that are extremely close in energy (~1 kcal/mol).

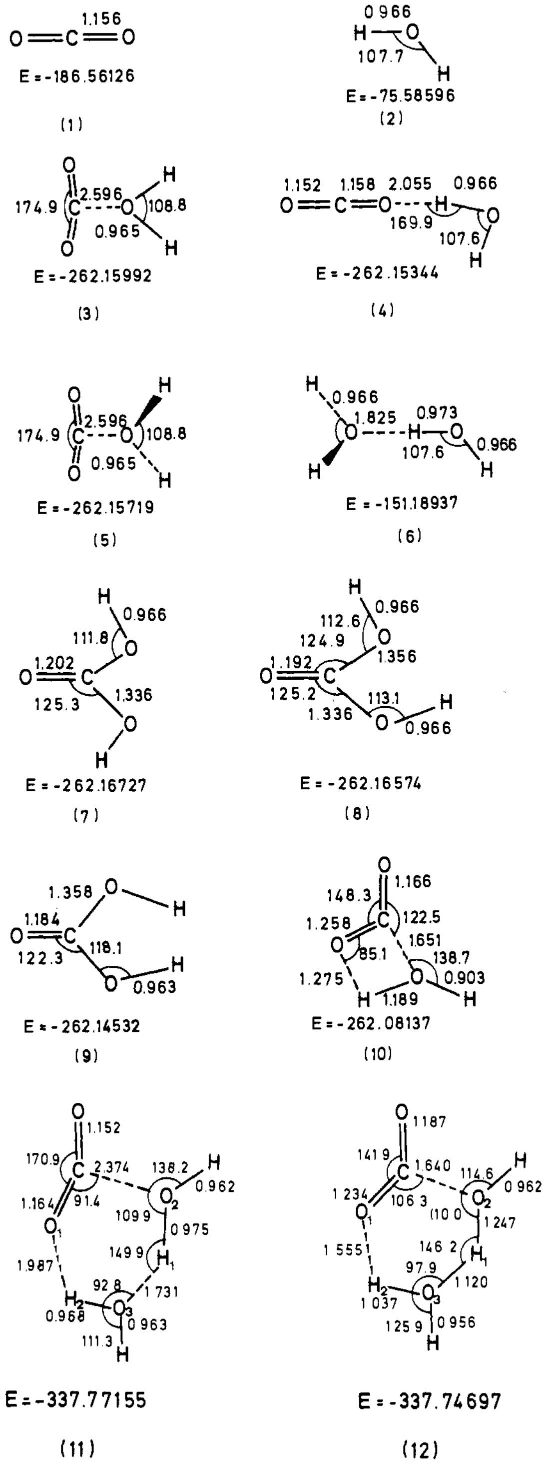

Figure 1. Optimized geometries and energies of the different structures that are relevant in the study of the $CO_2 + H_2O$ and $CO_2 + (H_2O)_2$ reactions. Energies are given in au, bond lengths in Å, and bond angles in deg.

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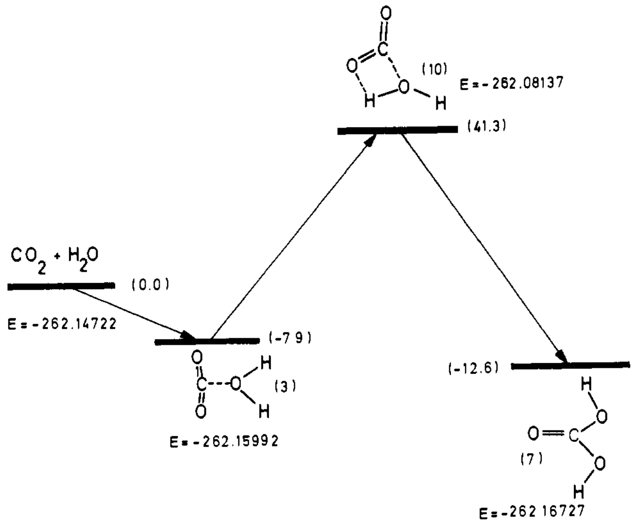

Figure 2. Relative energies of the $CO_2 + H_2O$ reaction (reaction 1) (kcal/mol). Values in parentheses refer to the numbering in Figure 1.

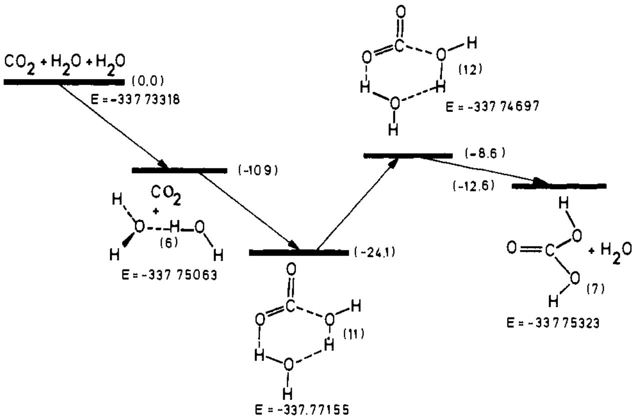

Figure 3. Relative energies of the $CO_2 + (H_2O)_2$ reaction (kcal/mol). Values in parentheses refer to the numbering in Figure 1.

III. The Hydration Reactions

The energy level diagram corresponding to the reaction of CO_2 with one water molecule is presented in Figure 2. The optimized structural parameters of transition state **10** are comparable to those obtained by Jönsson et al.[15] with a double-ζ basis set. We note a slight elongation of the O–H bond of H_2O in **10**, while in the transition state of the $CH_2{=}C{=}NH + H_2O$ addition reaction, for exemple, this bond was not changed at all, as shown previously.[7]

The transition state is found at 49.2 kcal/mol above that for the $H_2O{\cdot}CO_2$ complex. This result is comparable to the earlier calculated value of 55.9 kcal/mol,[5] but much higher than the experimental value of 17.7 kcal/mol.[13] The calculated activation energy is thus in the same order of magnitude as the activation barriers found for the intramolecular 1,3-proton-transfer reactions.[19,20] The reaction product, cis-trans conformation **8** of carbonic acid, lies ~53 kcal/mol lower than the transition state, and the heat of reaction $CO_2 + H_2O \rightarrow H_2CO_3$ (cis-trans) amounts to −11.6 kcal/mol. It has recently been shown, however, that this exothermic value may be an artefact due to basis set limitation.[17]

The reaction of CO_2 with two water molecules is schematically presented in Figure 3. The six-membered cyclic complex **11** is found at 24.1 and 13.2 kcal/mol below $CO_2 + 2H_2O$ and $CO_2 + (H_2O)_2$, respectively. By comparing the geometrical parameters between the six-membered complex **11** and the transition state **12**, it may be noted that the ring deformation is substantial. The $C{\cdots}O_2$ and $O_1{-}{-}{-}H_2$ distances between CO_2 and the water dimer become 0.734 and 0.432 Å shorter in the transition state, respectively, and within the water dimer, the intermolecular distance $O_3{\cdots}H_1$ becomes 0.61 Å shorter and the distance $O_2{\cdots}H_1$ becomes 0.272 Å longer. The HOH angles in both water monomers become 14.6 and 23.5° larger in transition state **12** compared to those of stable complex **11**. The $C{\cdots}O_2$ and $O_1{\cdots}H_2$ distances in the transition states are slightly smaller than the values found in the reaction $CH_2{=}C{=}O + (H_2O)_2$; 1.732 and 1.730 Å, respectively, with the STO-3G basis set.[21]

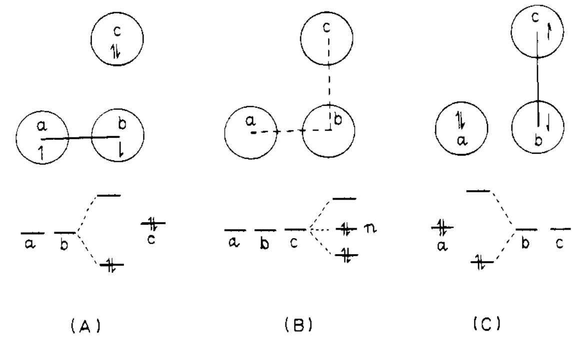

Figure 4. Schematic representation of the 3-orbital 4-electron interaction arising from the approach of a lone pair (in the c orbital) to the a–b bond. From A over B to C, the relative distance between c and b decreases with respect to the a–b distance. In B n is the nonbonding orbital arising from the interaction between the three basis orbitals.

The difference in energy between complex **II** and transition state **12** is calculated as only 15.5 kcal/mol while the corresponding energy difference between **3** and **10** of Figure 2 was more than three times as large. This stabilization of approximately 35 kcal/mol will of course be offset to some extent by the fact that **10** will be favored over **12** by entropy effects. Yet, the magnitude of the stabilization is such that a significant positive catalysis can be expected from the addition of a second water molecule. It is also well to observe that the calculated barrier of 15.5 kcal/mol is of the same magnitude as the experimentally determined activation energy of 17.7 kcal/mol. The energy of the reaction products (trans-cis conformer **8** of carbonic acid plus water) is found to lie only 5 kcal/mol below that of transition state **12**. It should be noted that these values are obtained from the calculations employing the split-valence basis set 3-21G; the inclusion of the polarization functions to the basis set and the electron correlation effect could modify them, but the energy diagram should still be qualitatively correct. Indeed, a recent extensive ab initio study[22] on a reaction of the same type as those considered in this present work ($NH_3 + HCOOH \rightarrow HCONH_2 + H_2O$) emphasized that correlation and polarization effects on the activation energy act in opposite directions. This study has shown that results obtained from the split-valence basis set calculations are consistent with those obtained from higher level calculations such as MP4/6-31G**.

A similar comprehensive theoretical study of the nucleophilic addition to the carbonyl group, especially the hydration of $H_2C{=}O$, has recently been reported.[8,9] By introducing a second water molecule, the proton transfer and the nucleophilic bond formation occurred simultaneously rather than energetically unfavorable proton transfer alone. Thus, along with the catalytic effect of the cationic binding sites such as NH_4^+ shown in an earlier work,[23] the catalytic effect of the second molecule of water is well documented.[7-9,21,27]

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Table I. Overlap Populations at Some Selected Points along the Reaction Pathway for the Reaction of Carbon Dioxide Plus the Water Dimer (3-21G Basis Set)

structure	$O_1 \cdots C$	$C \cdots O_2$	$O_2 \cdots H_1$	$H_1 \cdots O_3$	$O_3 \cdots H_2$	$H_2 \cdots O_1$
CO_2 (1) + $(H_2O)_2$ (6)	0.503	0.000	0.248	0.050	0.263	0.000
complex **11**	0.465	0.036	0.265	0.052	0.250	0.028
transition state **12**	0.350	0.122	0.123	0.131	0.181	0.091
H_2CO_3 (8) + H_2O (2)	0.202	0.217	0.000	0.265	0.000	0.267

As a possible rationalization of these results, we consider the ionization process of water and the water dimer:

$$H_2O \rightarrow H^+ + OH^- \tag{3}$$

and

$$(H_2O)_2 \rightarrow H_3O^+ + OH^- \tag{4}$$

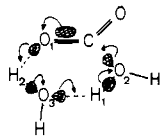
Figure 4 shows a three-orbital four-electron interaction. In the two extreme cases A and C, we have one bond and one lone pair. In the intermediate case B, we still have one essentially nonbonding orbital n, which is a linear combination of a and c (at the Hückel level of approximation, the coefficient of b is strictly zero). So, along the entire reaction path, one nonbonding orbital is conserved and its composition changes gradually from pure c to pure a. This process is clearly allowed and corresponds to a formal charge transfer from c to a. An exemple of this type of interaction is reaction 4 where in Figure 4A, for instance, c is an oxygen lone pair orbital, a is an oxygen bond orbital, and b is a hydrogen is orbital. If the focus is on the nuclear reaction coordinate, the process may of course also be designated as a proton transfer. In constrast, reaction 3 is a forbidden process, as it implies the transfer of two electrons from a bonding to a nonbonding orbital.

From an energetic point of view, both ionization processes 3 and 4 are highly endothermic, but the heat of reaction of the latter (~240 kcal/mol in 3-21G) is appreciably smaller than that of the former (~420 kcal/mol).

The geometrical parameters of transition state **12** (elongation of O_2–H_1 and reduction of O_3–H_1) appear to indicate that, in this state, the water dimer acts under its ionized form $H_3O^+ \cdot OH^-$. By the formation of H_3O^+ and OH^- from $(H_2O)_2$, which is an allowed process, the solvent may thus be transformed into a bifunctional (acid–base) catalyst, where the facile addition of OH^- to the carbon atom (without activation barrier)[24] is even more faciliated by the simultaneous capture of the excess charges by the H_3O^+ ion. In summary, the catalyzed reaction 2 is favored by the facility of the nucleophilic agent formation and the proton transfer in the water dimer.

From orbital symmetry consideration, it is also evident that for the addition of one H_2O the hydration is a forbidden 2 + 2 cycloaddition and thus has a high barrier. When the extra water is included, it becomes a 2 + 4 (allowed) cycloaddition with a low barrier.

The analysis of the evolution of the charge centroids of the localized orbitals which were performed by using the method of Foster–Boys[25] shows that the reorganization of the electron pairs along the hydration pathway of carbon dioxide by the water dimer occurs as follows:



$$n(O_2) \longrightarrow \sigma(CO_2)$$
$$\pi(CO_1) \longrightarrow n(O_1)$$
$$n(O_1) \longrightarrow \sigma(O_1H_2)$$
$$\sigma(O_3H_2) \longrightarrow n(O_3)$$
$$n(O_3) \longrightarrow \sigma(O_3H_1)$$
$$\sigma(O_2H_1) \longrightarrow n(O_2)$$

This cyclic electron movement is found to be the same as that observed with the addition of the water dimer to the C=O bond of ketene $H_2C{=}C{=}O$.[21]

At transition state **12**, the amount of the charge transfer is calculated at about 0.26 e from the water dimer toward carbon dioxide. The overlap populations of the six bonds which form the six-membered ring are collected in Table I. We note that at transition state **12**, the new bonds C–O_2, O_1–H_2, and O_3–H_1 are already appreciably but unequally formed. Thus, the transformation of stable complex **11** to H_2CO_3 + H_2O may be considered as a concerted but asynchronous process.

In conclusion, the calculated energy pathway for the reaction of carbon dioxide with the water dimer is clearly favored over that with one molecule of water and more closely approximates the experimental results found in aqueous solutions. This study also shows, for the first time, that there exits a quite stable six-membered ring complex made up of carbon dioxide and the water dimer which lies about 24 kcal/mol below the CO_2 + H_2O + H_2O system. It appears that this complex plays an essential role in the hydration reaction of carbon dioxide permitting a "preassociation mechanism"[26] where the reactants are oriented in an optimal manner creating the most favorable spatial and electronic conditions for a proton transfer in a rapid and concerted subsequent step.

Finally, the hydration with the water dimer constitutes, on the other hand, a case of active solvent catalysis where the solvent molecules participate actively as the catalyst in the chemical process.

Acknowledgment. The authors wish to acknowledge Prof. L. G. Vanquickenborne for constantencouragement and stimulating discussions. We also thank Dr. F. Volatron for critical reading of the manuscript. One of us (M.T.N.) is indebted to the Belgiam (Programmatie van het Wetenschapsbeleid) for financial support.

Registry No. Carbon dioxide, 124-38-9; carbonic acid, 463-79-6.