Synergism of Catalysis and Reaction Center Rehybridization. A Novel Mode of Catalysis in the Hydrolysis of Carbon Dioxide[‡]

Michael Lewis and Rainer Glaser*

Contribution from the Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211

Received: March 25, 2003

A quantum mechanical study is presented of the activation barrier of the one-, two-, and three-water hydrolyses of CO_2. Geometries were optimized, frequencies were calculated, and NPA charges were determined at MP2(full)/6-31G* and MP2(full)/6-311G**, and energies were also determined at MP4(full,SDTQ)/6-311G**// MP2(full)/6-311G** and QCISD(T)/6-31G**//MP2(full)/6-31G**. The activation barriers are $\Delta H_0 = 223.0$ kJ/mol and $\Delta G_{298} = 235.6$ kJ/mol for the one-water hydrolysis and they are $\Delta H_0 = 149.8$ kJ/mol and $\Delta G_{298} = 164.4$ kJ/mol for the two-water hydrolysis at MP4(full,SDTQ)/6-311G**. The catalytic effect of the second water molecule is due to the alleviation of ring strain in the proton-transfer transition state. The placement of the third water molecule in the proton-transfer ring causes only an insignificant catalytic effect with respect to the two-water hydrolysis. The placement of the third water molecule opposite the site of proton transfer is explored here and it leads to activation barriers of $\Delta H_0 = 122.6$ kJ/mol and $\Delta G_{298} = 143.1$ kJ/mol. The catalytic effect of the third water molecule is approximately 20 kJ/mol with respect to the two-water hydrolysis, and this is attributed to charge relaxation and rehybridization in the transition state. The results are compared to studies on the three-water hydrolysis of carbodiimide to discern the effects of atomic polarizability on the activation barriers of the hydrolyses of heterocumulenes. The conceptional insights predict that the catalytic effect should increase with more polarizable heteroatoms.

Introduction

The hydrolysis of carbon dioxide in carbonic anhydrase has long been an active area of research due to its fundamental importance for life.[1,2] The nonenzymatically catalyzed reaction has also received experimental[3−5] and theoretical attention.[6−12] The experimentally measured activation energy of 74.1 kJ/mol[5] has yet to be reproduced via quantum mechanical calculations. The main problem associated with the calculation of an accurate activation energy is the lack of a sufficient model for the description of the transition state. It is well-known that the hydrolysis of carbon dioxide in solution proceeds with catalysis from the solvent;[3] however the structure of the transition state in this water-catalyzed hydration remains unclear. Early self-consistent field calculations investigated the addition of one water molecule to one carbon dioxide molecule using a (7s3p, 4s1p) [4s2p, 2s1p] basis set, and an activation barrier of 233.9 kJ/mol was determined.[11] One reason for this much too high calculated activation energy certainly is the ring strain associated with the four-membered cyclic transition state, and this problem was addressed in later theoretical studies by including a second water molecule in the calculations.[10] This second water molecule functions as a proton shuttle and allows for the formation of an essentially strain-free six-membered cyclic transition state structure. At the modest HF/3-21G level of theory, the inclusion of this proton shuttle gave an activation barrier of 64.5 kJ/mol in excellent agreement with experiment. The second water molecule was described as catalyzing the hydration because the activation energy was reduced by over 138 kJ/mol with respect to the hydrolysis by a single water. The calculations were repeated, however, at higher levels of theory, and the activation energy rose quite substantially. The activation barriers ΔE_0 and ΔG_{298} are 135.1 and 169.9 kJ/mol, respectively, at the MP2/6-31G**//HF/6-31G** level.[8] Thus, the energies calculated at the lower level of theory were underestimated due to deficiencies in the theoretical method and choice of the basis set. Recent higher level theoretical studies have shown that the activation barrier for the hydrolysis of carbon dioxide with two water molecules is in fact higher than was initially proposed, whereas the second water molecule still was responsible for a catalytic effect of approximately 71 kJ/mol.[6]

The hydrolysis of carbon dioxide with two water molecules via a six-membered cyclic transition state structure does not adequately describe the activation. The calculated ΔE_0 and ΔG_{298} values are significantly higher than the experimental value and, thus, there must exist another mode of solvent catalysis that contributes to the lowering of the activation energy. The effects of a third and fourth water molecule added to the site of proton transfer have been studied theoretically, and the results showed little decrease in the activation energy.[7] With respect to the hydration involving two water molecules, the consideration of a third water molecule at the active site (Scheme 1, A) decreased the ΔE_0 activation energy merely by 5.0, 10.9, and 4.2 kJ/mol, respectively, at the levels MP2/6-31G**, MP2/6-311++G**, and QCISD(T)/6-31G**. Likewise, the subsequent addition of a fourth water molecule in the proton transfer chain also had little catalytic effect. It appears that a six-membered cyclic transition state is sufficient for the proton transfer to occur essentially strain-free and any additional water molecules at the site of proton transfer have but a negligible effect on the energy of activation.

Catalysis in the Hydrolysis of Carbon Dioxide

J. Phys. Chem. A, Vol. 107, No. 35, 2003 **6815**

SCHEME 1: Two Possibilities for the Hydrolysis of Carbon Dioxide by Three Water Molecules

A   **B**
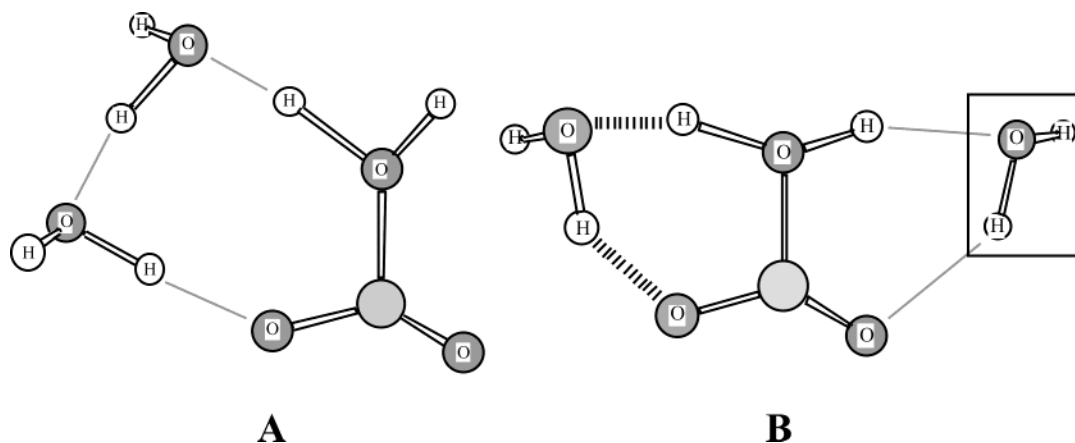
A mode of catalysis that may contribute to the lowering of the activation energy is the placement of a third water molecule *opposite* the site of proton transfer, as described by B (Scheme 1). We have previously proposed a mechanism for the hydrolysis of the parent carbodiimide (HN=C=NH) where a structure similar to B resulted in an additional 38.5 kJ/mol of catalysis with respect to the hydration with two water molecules.[13] This catalytic effect was almost equivalent to the 48.5 kJ/mol of catalysis generated from addition of a second water molecule! In the present article, we extend our model to the hydration of carbon dioxide. Several pertinent issues are addressed in the process. First, we will discern the catalytic effect of structure B, in an attempt to bring the theoretically calculated activation energy into better accord with experiment. Second, this study provides insights into catalytic effects associated with differential charge changes, which are rather difficult to predict. It is clear that the oxygen atom is more electronegative than the nitrogen atom but this information does not say anything about which atoms will carry more negative charge in a molecule. In fact, the less electronegative N atom carries a much higher negative charge in carbodiimide than the corresponding O atom in carbon dioxide simply because of its connectivity environment.[13] If one is interested in catalytic effects, then one needs to go one step further and inquire about the likelihood of atomic charge changes. In the present case, one of these questions would be: Will the higher negative charge of the N atom in the NH^R group increase more than the lower negative charge on the O atom of the carbonyl O^R atom? To answer this kind of question a priori requires information about changes in atom electronegativity as a function of charge, and that relation is hard to impossible to predict, as it depends on connectivity. Another complicating factor relates to the polarizability changes that are associated with differential charge changes. The catalytic effect exerted by the spectator water molecule is due to H-bonding, which is mostly an electrostatic interaction and subject to mutual polarization. The experimental dipole polarizability of the O atom is $(0.77 \pm 0.06) \times 10^{-24}$ cm^3 and that of the N atom is $(1.13 \pm 0.06) \times 10^{-24}$ cm^3.[14] In atomic units, these values are 5.2 ± 0.4 and 7.6 ± 0.4, respectively. Thus, the N atom is approximately 50% more polarizable than the O atom. But how does the polarizability of an N atom that is very negatively charged compare to the polarizability of an O atom that is much less charged? Again, one cannot say and accurate computations are needed to shed light on the issue. Here, we discuss the differential charge changes associated with proton-transfer reactions in hydrogen bonded systems and discuss their effects on activation barriers. The hydrolyses of carbon dioxide and of

the parent carbodiimide are excellent examples to illustrate such effects.

Computational Methods

All structures were optimized and vibrational analyses were performed at the MP2(full)/6-31G*, MP2(full)/6-31G**, and MP2(full)/6-311G** levels of theory[15] using the Gaussian quantum-mechanical program.[16] Single-point calculations were performed at the MP4(full,SDTQ)/6-311G** level for the MP2(full)/6-311G**-optimized structures and at the QCISD(T)/6-31G** level for the MP2(full)/6-31G**-optimized structures. The MP2(full)/6-31G** and QCISD(T)/6-31G** calculations were performed to allow for a direct comparison with previous calculations of the three water hydrolysis of carbon dioxide that placed the third water molecule in the proton-transfer ring. The reported activation barriers ΔH_0 include vibrational zero-point energy corrections that were scaled by the empirical value 0.9646,[17] and the reported activation Gibbs free energies ΔG_{298} include the thermochemical and entropy components.[18] Populations were computed for each structure using the natural population analysis (NPA).[19]

Results and Discussion

Catalysis by Proton Shuttle. The calculated van der Waals complexes and transition state structures (Figure 1, **1**−**4**) for the hydrolyses of carbon dioxide with one and two water molecules gave activation energies ΔH_0 (Table 1, Figure 2) that are in good agreement with previous calculations.[6,8] At the MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** level the activation energies ΔH_0 for the hydrolyses with one and two water molecules are 223.0 and 149.8 kJ/mol (Figure 2), respectively. At the level of theory previously employed by Nguyen,[7] QCISD(T)/6-31G**//MP2(full)/6-31G**, the activation energies for the one- and two-water hydrolyses of carbon dioxide are $\Delta H_0 = 212.6$ kJ/mol and $\Delta H_0 = 224.6$ kJ/mol, respectively. The catalytic effect due to the addition of the second water molecule, on the ΔH_0 potential energy surface (Figure 2), is 73.2 kJ/mol at MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** and 79.2 kJ/mol at QCISD(T)/6-31G**//MP2(full)/6-31G** (Table 1).

Reaction Center Rehybridization and Charge Relaxation. The placement of the third water molecule at the position shown in B can be rationalized by structural and electronic differences between the transition states **2** and **4** of the hydrolyses with one and two water molecules. In the transition state structure, the bond formation between the oxygen of the adding water
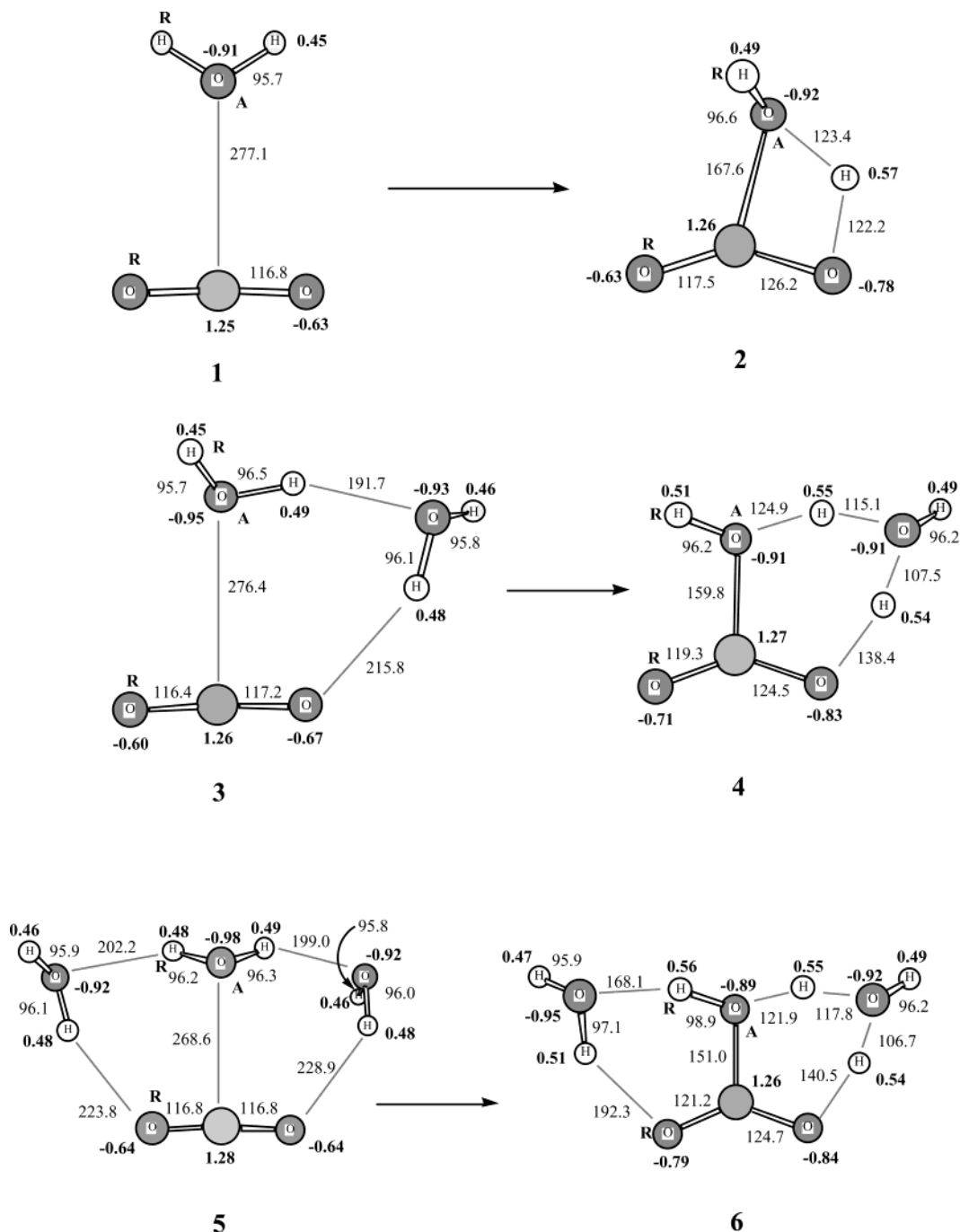
Figure 1. MP2(full)/6-311G**-optimized van der Waals complexes and transition state structures for the hydrolyses of carbon dioxide by one, two, and three water molecules. Bond lengths are given in pm, and charges are in boldface.

TABLE 1: Activation Energies[a,b]

	hydrolysis by one water		hydrolysis by two water		hydrolysis by three water	
theoretical level	ΔH_0	ΔG_{298}	ΔH_0	ΔG_{298}	ΔH_0	ΔG_{298}
MP2(full)/6-31G* = A	214.2	227.4	133.1	146.4	99.2	115.8
MP2(full)/6-311G** = B	220.5	232.8	143.5	158.4	115.1	135.6
MP4(full,SDTQ)/6-311G**//B	223.0	235.6	149.8	164.4	122.6	143.1
MP2(full)/6-31G** = C	211.0	223.0	129.9	143.9	96.9	114.4
QCISD(T)/6-31G**//C	212.6	224.6	133.4	147.4	100.9	118.4

[a] Energies in kJ/mol. [b] Activation energies ΔH_0 include scaled (0.9646[17]) vibrational zero-point energies. [c] MP2(full)/6-311G** and CISD(T)/6-31G**//MP2(full)/6-31G** levels were used by Nguyen et al.[7]

(H_2O^A) and the C atom ($C-O^A$) has progressed more in **4** than in **2**; the transient CO bond is 7.8 pm shorter in **4** than in **2**. Furthermore, the rehybridization of the C atoms has advanced more in **4** than in **2** and this is illustrated by the ∠(O−C−O)

angles of 139.9° in **4** and of 145.7° in **2**. These structural differences during activation have important electronic consequences for the carbonyl O atom that *remains* a carbonyl O atom during the reaction (=O^R) and for the O^A−H bond that
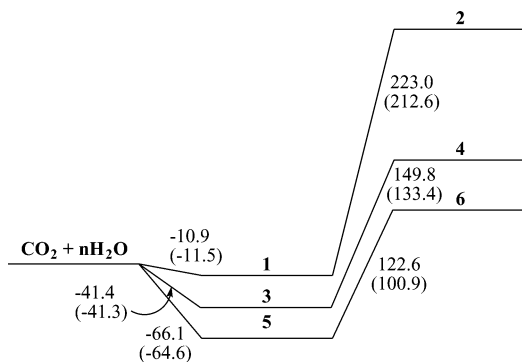
Catalysis in the Hydrolysis of Carbon Dioxide

J. Phys. Chem. A, Vol. 107, No. 35, 2003 **6817**

Figure 2. ΔH_0 activation barriers of the hydrolyses of carbon dioxide ($n = 1-3$). All energies are given in kJ/mol, calculated at the theoretical levels MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** and QCISD(T)/6-31G**//MP2(full)/6-31G** (in brackets) and including corrected[17] VZPE values.

TABLE 2: Atom Charges Determined by Natural Population Analysis

	CO$_2$			C(NH)$_2$				
	O^A	H^R	O^R	O^A	H^R	NH^R	N^R	H^R
1[a]	−0.97	+0.49	−0.64	−0.97	+0.50	−0.43	−0.84	+0.41
1[b]	−0.91	+0.45	−0.63					
2[a]	−0.96	+0.53	−0.64	−0.97	+0.51	−0.42	−0.84	+0.42
2[b]	−0.92	+0.49	−0.63					
3[a]	−1.01	+0.48	−0.62	−1.02	+0.49	−0.33	−0.80	+0.47
3[b]	−0.95	+0.45	−0.60					
4[a]	−0.95	+0.54	−0.73	−0.91	+0.53	−0.52	−0.90	+0.38
4[b]	−0.91	+0.51	−0.71					
5[a]	−1.04	+0.51	−0.66	−1.03	+0.49	−0.31	−0.79	+0.48
5[b]	−0.98	+0.48	−0.64					
6[a]	−0.94	+0.58	−0.80	−0.87	+0.59	−0.63	−1.01	+0.38
6[b]	−0.89	+0.56	−0.79					

[a] MP2(full)/6-31G*. [b] MP2(full)/6-311G**.

TABLE 3: Change in Atomic Charges in Proceeding from the Precoordination Complexes to the Transition States of the Hydrolyses of Carbon Dioxide and Carbodiimide

	δ(O^A)		δ(H^R)		δ(X^R)[c]	
reaction	L1[a]	L2[b]	L1[a]	L2[b]	L1[a]	L2[b]
1 → 2, CO$_2$	+0.01	−0.01	+0.04	+0.04	0.00	0.00
1 → 2, C(NH)$_2$	0.00		+0.01		+0.01	
3 → 4, CO$_2$	+0.06	+0.04	+0.06	+0.06	−0.11	−0.11
3 → 4, C(NH)$_2$	+0.11		+0.04		−0.19	
5 → 6, CO$_2$	+0.10	+0.09	+0.07	+0.08	−0.14	−0.13
5 → 6, C(NH)$_2$	+0.16		+0.10		−0.32	

[a] Theoretical level L1 = MP2(full)/6-31G*. [b] Theoretical level L2 = MP2(full)/6-311G**. [c] X = O^R and X = NH^R for the hydrolyses of carbon dioxide and of carbodiimide, respectively.

remains bonded during the reaction (O^A−H^R). Hybridization concepts would suggest that a carbonyl O atom in carbon dioxide would be less negative than the O atom in carbonic acid.[20] Thus, we would predict that the change in charge of O^R would be more negative for **3 → 4** than for **1 → 2**. This hypothesis was confirmed by natural population analyses of **1−4** (Tables 2 and 3), which showed Δq(O^R) values of 0.00 and −0.11 for **1 → 2** and **3 → 4**, respectively. In a similar construct, the water molecule is being converted into an alcohol in the course of the reaction, and one would expect the −OH group in an alcohol to be overall less negative than the −OH group in water.[21] Therefore, Δq(O^A−H^R) should be more positive for **3 → 4** than for **1 → 2**. This is manifested in the NPA analyses of **1−4** and, moreover, there is a greater loss of electron density for both O^A and H^R in the process **3 → 4** (Δq(O^A) = +0.06;

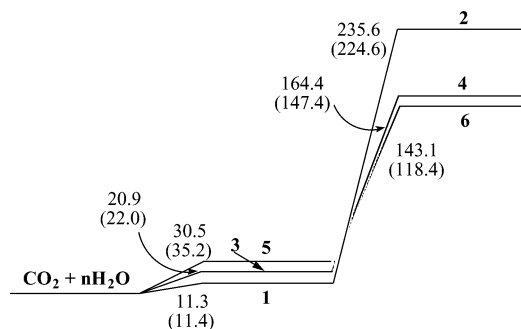**Figure 3.** ΔG_{298} activation barriers of the hydrolyses of carbon dioxide ($n = 1-3$). All energies are given in kJ/mol, calculated at the levels MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** and QCISD(T)/6-31G**//MP2(full)/6-31G** (in brackets). Thermodynamical data are computed at the MP2(full)/6-311G** level for the MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** calculations and at the MP2(full)/6-31G** level for the QCISD(T)/6-31G**//MP2(full)/6-31G** calculations.

Δq(H^R) = +0.06) than for **1 → 2** (Δq(O^A) = +0.01; Δq(H^R) = +0.04).

The electronic relaxations during the activation processes **1 → 2** and **3 → 4** show an enhanced ability to engage in H-bonding for both the O^A−H^R bond and the O^R atom in the case of the hydrolysis with two water molecules. The O^A−H^R group is a better H-bond donor because the negative charge on O^A is diminished and the positive charge on H^R is increased. The =O^R atom is a better H-bond acceptor because it is more negatively charged. These effects should be manifested in any H-bonding environment and the hydrolysis with three water molecules, as described by B, is the special case where H-bonding at both sites is accomplished by one water molecule.

Synergy between Proton-Shuttle Catalysis and Microsolvation. The optimized van der Waals complex, **5**, and the transition state structure, **6**, for the hydrolysis with three water molecules are shown in Figure 1. Table 1 and Figure 2 show that the addition of the third water molecule does indeed lower the activation barrier for the hydrolysis of carbon dioxide: The activation energy ΔH_0 is decreased to 122.6 kJ/mol at MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** and to 100.9 kJ/mol at the QCISD(T)/6-31G**//MP2(full)/6-31G** level. This represents catalytic effects of 27.2 and 32.5 kJ/mol at the two respective levels, when compared to the hydrolysis involving two water molecules, and catalytic effects of 100.4 and 111.7 kJ/mol with respect to the single-water hydrolysis. The catalytic effect of structure B is thus over 7 times as great as the effect of structure A![7] Note that the C−O^A bond in **6** is even shorter than in **4** and, in fact, all parameters indicate that all the structural and electronic changes associated with the processes **1 → 2** and **3 → 4** clearly are enhanced for **5 → 6**. *The catalytic effects of the second and third water molecules truly are synergetic.*

We also computed the Gibbs free energies of activation ΔG_{298} and these values can be seen in Table 1 and Figure 3. The pertinent activation barriers again are the energy differences between the precoordination complexes and the transition state structures. We stress again that it is not the purpose of our studies to model the tetramolecular gas-phase reaction. Instead, it is our goal to better understand the solution reaction. In solution, entropy is less of an issue because all molecules are aggregated at all times and in solution this reaction is basically a "unimolecular" reaction of an aggregate. Therefore, the precoordination complexes represent the smallest meaningful aggregates that allow one to model the situation in solution. At

TABLE 4: Differential Charge Changes[a,b]

reaction	$\delta\delta(O^A)$	$\delta\delta(H^R)$	$\delta\delta(= X^R)$[c]
3 → **4** CO_2	+0.05	+0.02	−0.11
3 → **4** HNCNH	+0.11	+0.03	−0.20
5 → **6** CO_2	+0.10	+0.04	−0.13
5 → **6** HNCNH	+0.16	+0.09	−0.33

[a] Changes in atomic charges in proceeding from the precoordination complexes to the transition states for the hydrolyses of CO_2 and HNCNH using two and three water molecules, **3** → **4** and **5** → **6**, respectively, relative to the hydrolyses of CO_2 and HNCNH with one water molecule, **1** → **2**. [b] Theoretical level L1 = MP2(full)/6-31G*. [c] X = O^R and X = NH^R for the hydrolyses of carbon dioxide and of carbodiimide, respectively.

the MP4(full,SDTQ)/6-311G**//MP2(full)/6-311G** level, the catalytic effect of the second water molecule is $\Delta G_{298} = 71.2$ kJ/mol whereas the third water molecule has an additional catalytic effect of $\Delta G_{298} = 21.3$ kJ/mol. At the QCISD(T)/6-31G**//MP2(full)/6-311G** level employed by Nguyen,[7] the catalytic effect of the second water molecule is $\Delta G_{298} = 77.2$ kJ/mol whereas the catalytic effect of the third water molecule is $\Delta G_{298} = 29.0$ kJ/mol. The catalytic effects clearly remain.

Differential Charge Changes. The catalytic effect of the second and third water molecules in the hydrolysis of carbon dioxide is not as great as it is for carbodiimide.[13] We have shown that stabilizing the charges in the transition state structures can lower the activation barriers for the hydrolyses of carbodiimide[13] and carbon dioxide. The hydrolyses of carbodiimide with two and three water molecules both show greater charge localization with respect to the hydrolysis by one water than the respective hydrolyses of carbon dioxide. Table 4 shows the differential changes in atomic charges between **3** → **4** and **1** → **2** and between **5** → **6** and **1** → **2** for the hydrolyses of carbon dioxide and carbodiimide.

In the hydrolysis of carbon dioxide with two water molecules, **3** → **4**, the O^R atom becomes 0.11 more negative than in the hydrolysis with one water, **1** → **2** (Table 4). For the hydrolysis of carbodiimide with two water molecules, however, the NH^R fragment becomes 0.20 more negative than in the hydrolysis with one water molecule. Likewise, the O^A and H^R atoms in the hydrolysis of carbon dioxide with two water molecules, **3** → **4**, become +0.05 and +0.02 more positive than in the hydrolysis with one water, **1** → **2** (Table 4). For the hydrolysis of carbodiimide with two water molecules, however, the O^A and H^R atoms become +0.11 and +0.03 more positive compared to the single-water hydrolysis of carbodiimide. The differential charge changes for the three water hydrolyses **5** → **6** show all of the exact same features and the changes all are *larger in magnitude* (Table 4). This finding is highly significant because it reveals the underlying electronic origin for the synergism of the catalytic effects associated with the proton shuttle and the microsolvation.

The charge relaxations associated with proceeding from the van der Waals complexes to the transition state structures of the hydrolyses with two or three water molecules is considerably greater for carbodiimide than for carbon dioxide. The substantially greater polarizability of the N atom allows the NH^R fragment of carbodiimide to take on more negative charge than O^R of carbon dioxide. Moreover, the intrinsic ability of the N atom to accumulate charge results in the O^A and H^R atoms becoming more positive for the two- and three-water hydrolyses

of carbodiimide than for two- and three-water hydrolyses of carbon dioxide. Thus, the increased charge localization in the hydrolyses of carbodiimide with respect to the hydrolyses of carbon dioxide is directly related to the higher polarizability of nitrogen. Therefore, the catalytic effect of a third water molecule, as placed in B, is related not only to the electronegativity but also to the polarizability of the heteroatom present in the heterocumulene. This trend suggests that the catalytic effect should increase with more polarizable heteroatoms.

References and Notes

(1) Merz, K. M.; Banci, L. *J. Am. Chem. Soc.* **1997**, *119*, 863−871.
(2) Christianson, D. W.; Fierke, C. A. *Acc. Chem. Res.* **1996**, *29*, 331−339.
(3) Terlouw, J. K.; Lebrilla, C. B.; Schwarz, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 354−355.
(4) Marlier, J. F.; O'Leary, M. H. *J. Am. Chem. Soc.* **1984**, *106*, 5054−5057.
(5) Magid, E.; Turbeck, B. O. *Biochim. Biophys. Acta* **1968**, *165*, 515−524.
(6) (a) Loerting, T.; Tautermann, C.; Kroemer, R. T.; Kohl, I.; Hallbrucker, A.; Mayer, E.; Liedl, K. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 892−894. (b) Hage, W.; Liedl, K. R.; Hallbrucker, A.; Mayer, E. *Science* **1998**, *279*, 1332−1335. (c) Liedl, K. R.; Sekusak, S.; Mayer, E. *J. Am. Chem. Soc.* **1997**, *119*, 3782−3784.
(7) Nguyen, M. T.; Raspoet, G.; Vanquickenborne, L. G.; Van Duijnen, P. T. *J. Phys. Chem. A* **1997**, *101*, 7379−7388.
(8) Merz, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 7973−7980.
(9) Liang, J.-Y.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1986**, *108*, 5051−5058.
(10) Nguyen, M. T.; Ha, T.-K. *J. Am. Chem. Soc.* **1984**, *106*, 599−602.
(11) Jonsson, N.; Karlstrom, G.; Wennerstrom, H.; Forsen, S.; Roos, B.; Almlof, J. *J. Am. Chem. Soc.* **1977**, *99*, 4628−4632.
(12) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *Aust. J. Chem.* **1972**, *25*, 1601−1612.
(13) (a) Lewis, M.; Glaser, R. *J. Am. Chem. Soc.* **1998**, *120*, 8541−8542. (b) Lewis, M.; Wu, Z.; Glaser, R. *J. Phys. Chem. A* **2000**, *104*, 11355−11361. (c) Glaser, R.; Lewis, M.; Wu, Z. *J. Phys. Chem. A* **2002**, *106*, 7950−7957. (d) Glaser, R.; Wu, Z.; Lewis, M. *J. Mol. Struct.* **2000**, *556*, 131−141. (e) Lewis, M.; Glaser, R. *Chem. Eur. J.* **2002**, *11*, 1934−1944.
(14) Alpher, R. D.; White, D. R. *Phys. Fluids* **1959**, *2*, 153−161.
(15) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.
(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*, revision C.3; Gaussian Inc.: Pittsburgh, PA. 1995.
(17) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345−350.
(18) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc.: Pittsburgh, PA, 1996.
(19) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628−646.
(20) NPA calculations on MP2(full)/6-311G**-optimized structures show that the population of the O atom in carbon dioxide is −0.61, and it is −0.74 in carbonic acid.
(21) NPA calculations on MP2(full)/6-311G**-optimized structures show that the population of an OH group in water is −0.45, and it is −0.24 in carbonic acid.