

# Water-Assisted Dissociation Reactions for the Compounds of A(CO)B and A(CO)<sub>2</sub>B (A, B = H, OH): A Density Functional Theory Study

Chiu-Ling Lin and San-Yan Chu\*

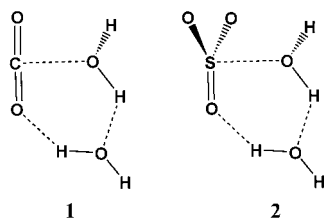
Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, ROC

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**Abstract:** Dissociation reactions of mono- and dicarbonyl compounds, A(CO)B and A(CO)<sub>2</sub>B (A, B = H, OH), to form CO, CO<sub>2</sub>, H<sub>2</sub>O, or H<sub>2</sub>, were studied theoretically by the B3LYP/6-31G\*\* method. We found that the participation of water can modify the reaction forbiddenness in addition to providing strain relief for the transition structure. It appeared that the water-assisted reactions are more effective for the monocarbonyl series than for the dicarbonyl series. Because the bonding of the hydrogen atom is less directional, the transition structure of a dehydrogenation reaction is less strained and thus receives a less strain relief effect than the dehydration reaction of the same ring size. A substantial increase in asynchronicity between the two leaving groups was observed from the water-free to the water-assisted reactions.

## Introduction

It is now well-established that in the reactions H<sub>2</sub>O(g) + SO<sub>3</sub>(g) → H<sub>2</sub>SO<sub>4</sub>(g) and H<sub>2</sub>O(g) + CO<sub>2</sub>(g) → H<sub>2</sub>CO<sub>3</sub>(g), the presence of a second H<sub>2</sub>O molecule can lower the reaction barrier effectively, and thus make the reactions more feasible.<sup>1–18</sup> The transition structures with an additional H<sub>2</sub>O molecule are characterized by less strained six-membered rings (**1**, **2**).



The second H<sub>2</sub>O molecule serves both as a proton acceptor and donor to facilitate the reaction. The water-assisted hydration is

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expected to be rather general if the transition state of the original hydration reaction is strained. Several groups have found similar reaction on keteneimine,<sup>19</sup> ketene,<sup>20</sup> formaldehyde,<sup>21</sup> and many other systems.<sup>22</sup>

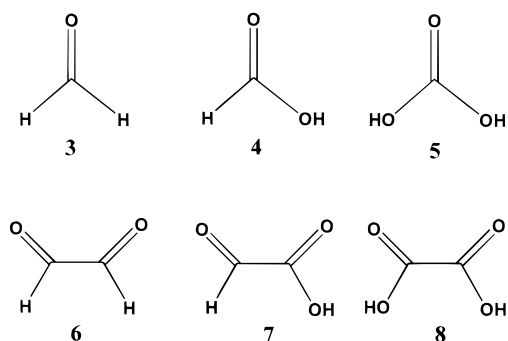
Certainly more water molecules can also participate in a chain relay process. The question of the actual number of water molecule involved is difficult to answer. Nguyen<sup>17</sup> showed theoretically that in the hydration of CO<sub>2</sub>, the second water lowers the barrier by 17.70 kcal/mol in comparison the third water of 2.63 kcal/mol. It may be an indication of a convergence with respect to the third water,<sup>23</sup> and it is doubtful the transition state with one more water molecule is stable enough in the solvent environment. In this work we restrict our study to the catalytic effect of the second water on a variety of carbonyl systems (Chart 1).

The main interest of this work is to examine the catalytic effects on the transition structure such as asynchronicity and partial charge for the two leaving groups. We also look into some differences between the dehydrogenation and the dehydration reactions such as forbiddenness and strain.

Since the catalytic effect operates in both the forward and backward directions, we choose to study the reverse reaction, the dissociation reaction, for the monocarbonyl system [formaldehyde (H<sub>2</sub>CO, **3**),<sup>24</sup> formic acid (HCOOH, **4**),<sup>25–28</sup> and

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Chart 1



carbonic acid ( $\text{H}_2\text{CO}_3$ , **5**)<sup>16–18</sup> and the dicarbonyl system [glyoxal ( $\text{H}(\text{CO})(\text{CO})\text{H}$ , (**6**)<sup>29–32</sup> glyoxylic acid ( $\text{HO}(\text{CO})(\text{CO})\text{H}$ , **7**),<sup>33–35</sup> and oxalic acid (**8**)].<sup>36–38</sup> Specifically, the dehydration reactions for compounds **4**, **5**, **7**, and **8** and the dehydrogenation reactions for compounds **3**, **4**, **6**, and **7** are the focus of this study. These reactions are nearly isenthalpic ( $\Delta H \approx 0$ ) for the same number of bonds for the dissociation products as for the reactants. We will show that for the monocarbonyl systems, the  $\text{H}_2\text{O}$  molecule is indeed an effective catalyst, lowering the activation energy by more than 20 kcal/mol. However, we find that the  $\text{H}_2\text{O}$  molecule is not so helpful for the dicarbonyl systems. At first sight this seems surprising since the  $\text{H}_2\text{O}$  molecule is expected to be similarly effective in strain relief in both cases. Therefore we expect that besides the geometrical effect, some electronic effect also plays an important role.

### Computational Method

All calculations presented here were done with the GAUSSIAN94 program.<sup>39</sup> All equilibrium geometries and transition structures were fully optimized, without any symmetry constraints. The density functional method used in this work combines Becke's hybrid three-parameter exchange functional with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP), which has been shown to be quite reliable in calculating both geometry and energy with semiquantitative accuracy.<sup>40</sup> The standard 6-31G\*\* basis set that includes d- and p-type polarization functions on non-hydrogen and hydrogen atoms, respectively, was used. Therefore, the calculations are denoted by B3LYP/6-31G\*\*. Also, all stationary points obtained

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in the optimization process were characterized by frequency calculations. Zero-point vibrational corrections (ZPE) obtained from frequency calculations were added to the total energies.

The bond order used in our analysis is the overlap-weighted NAO (natural atomic orbital) bond order. It is the sum of off-diagonal NAO density matrix elements between atoms multiplied by the corresponding PNAO overlap integral.<sup>41</sup>

### Results and Discussions

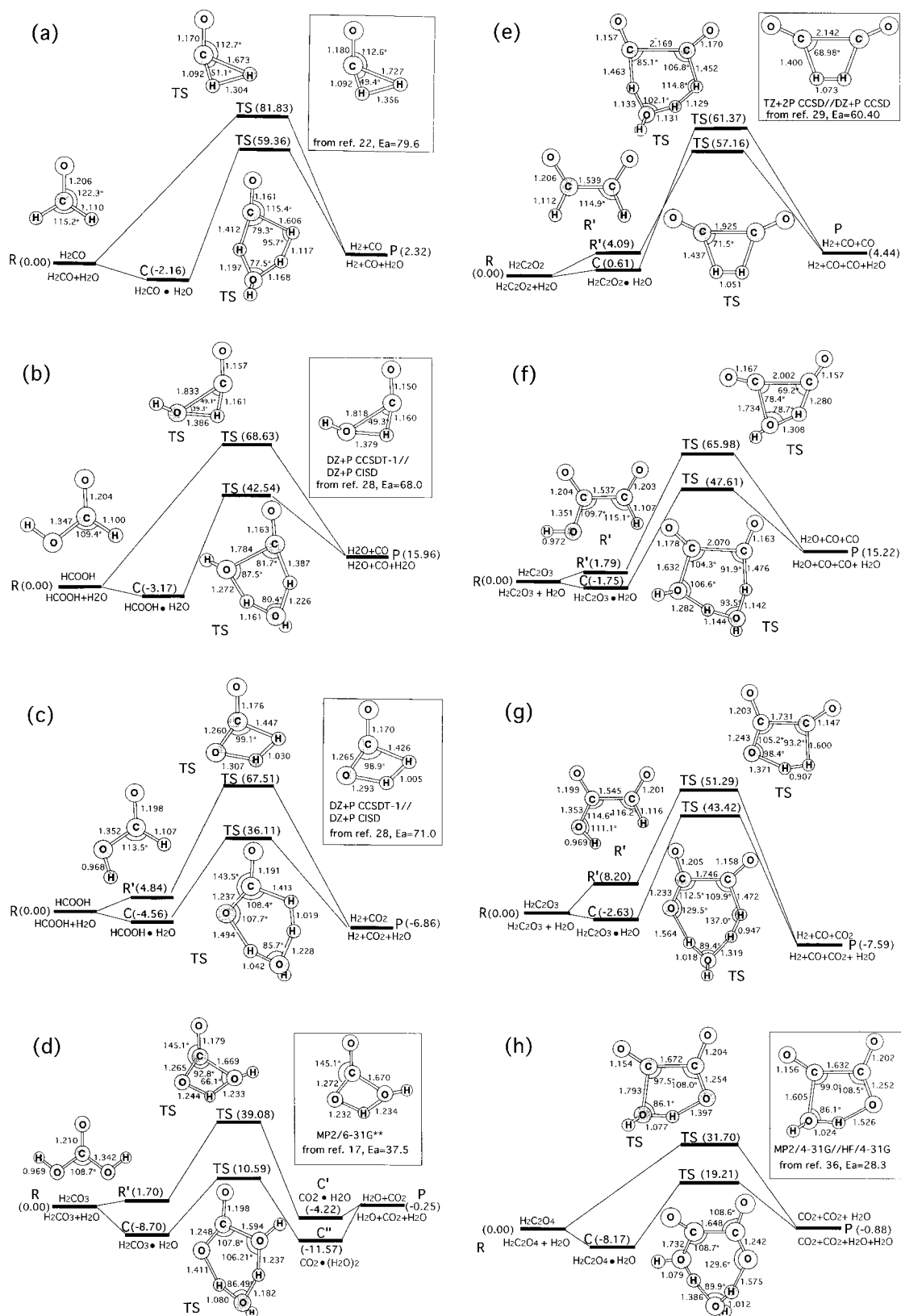
**(I) Activation Energy Lowering.** The calculated energy profiles for the dissociation reactions of compounds **3–8**, both with and without the assistance by a  $\text{H}_2\text{O}$  molecule, are presented graphically in Figure 1a–h. The zero-energy is assigned to the reactant (**R**) (or reactant plus  $\text{H}_2\text{O}$  at infinite separation for the water-assisted reaction). A complex is formed between the reactant and water molecules. Relative energies in (kcal/mol) are given for the complex (**C**), transition state (**TS**), and products (**P**). The geometries of the transition states are shown in comparison with some available published results, which were usually obtained by using a comparable basis set, but with a different approach, such as the Møller–Plesset method.<sup>17</sup> The agreement between our results and the published results gives us confidence about our B3LYP/6-31G\*\* method. Our main interest is to derive some general qualitative rules on the trends in both series of reactants, especially for the reaction with vs without  $\text{H}_2\text{O}$ . Therefore, we have not carried out the calculations with a more extended basis, or a more sophisticated theory, expecting that it will not significantly modify our conclusion.

The lowering in activation energies, defined as  $\Delta E_a = E_a(\text{with } \text{H}_2\text{O}) - E_a(\text{without } \text{H}_2\text{O})$ , is given in Table 1 ( $E_a$  is defined with respect to the reactant, not the complex). We use the symbols **X'** and **X''** for the water-assisted dehydrogenation and dehydration, respectively, for the molecules **X**, as shown in Chart 2. The two bond angles in each system are for discussion later in section II. The corresponding quantities of free energies are also given in parentheses. Since the pattern of  $\Delta G$  is similar to that of  $\Delta E$  for the interest of this work, we will not discuss  $\Delta G$  further.

The complex energy between a water molecule and the reactant can be significant, especially for an ionic reactant. For the complex involving the polar neutral reactant  $\text{SO}_3$ , its complex with  $\text{H}_2\text{O}$  and the  $(\text{H}_2\text{O})_2$  cluster is 7.89 and 26.31 kcal/mol,<sup>5</sup> respectively. The interactions involving the carbonyl systems here are much weaker. Further, we are concerned with the dissociation rather than the addition reaction with the complex involving only one water molecule. Therefore the complex stabilization energy plays a minor role except for the systems **5''** and **8''** with two strong hydrogen bonds which total 8 kcal/mol.

The  $\Delta E_a$  values are significant for monocarbonyl systems. For dehydration reactions, the values are  $-26.09$  and  $-28.49$  kcal/mol for compounds **4** and **5**, respectively. For dehydrogenation reaction, the values are  $-22.47$  and  $-31.40$  kcal/mol for compounds **3** and **4**, respectively. However, for the dicarbonyl systems, the  $\Delta E_a$  values are generally smaller in magnitude. For the dehydration the values are  $-18.37$  kcal/mol for **7** and  $-12.49$  kcal/mol for **8**. In contrast, for the dehydrogenation reactions, the values are only  $+4.21$  and  $-7.87$  kcal/mol for **6** and **7**, respectively. Therefore the  $\text{H}_2\text{O}$  molecule is not so helpful in lowering the reaction barrier here, although it is still active in the modification of charge distribution (discussed later in section III).

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**Figure 1.** The B3LYP/6-31G\*\* with ZPE correction energy profiles for reactant (**R**), complex (**C**), transition state (**TS**), and product (**P**) and structures for **TS** in comparison with available published results in the frames. The dehydrogenation reactions are represented in (a) for compound **3** and **3'** (see Charts 1 and 2 for system definitions), (c) for **4** and **4'**, (e) for **6** and **6'**, and (g) for **7** and **7'** and the dehydration reactions in (b) for **4** and **4'**, (d) for **5** and **5'**, (f) for **7** and **7'**, and (h) for **8** and **8'**, respectively. (Energy is given in kcal/mol relative to **R** and bond distance in Å. For clarity and convenience of illustration, the energy levels were not drawn to scale.)

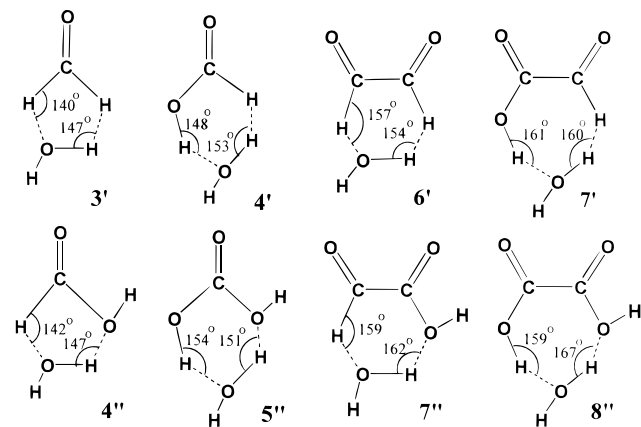
**(II) Ring Strain and Reaction Forbiddenness.** To appreciate the strain relief effect for the transition structure in water-assisted reaction, it is helpful to distinguish between the dehydration

and the dehydrogenation reaction. Since the bonding of hydrogen with the *s* orbital is nondirectional, the leaving hydrogen atom can form a new bond along any direction in the transition

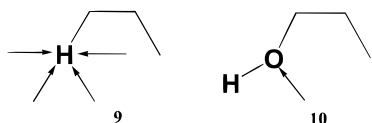
**Table 1.** The Energy Barrier<sup>a</sup> Lowering ( $\Delta E_a = E_a(\text{with H}_2\text{O}) - E_a(\text{without H}_2\text{O})$  in kcal/mol) for the Dehydrogenation and Dehydration Reactions

	monocarboxyl				dicarboxyl			
	H <sub>2</sub> CO		HCOOH		H <sub>2</sub> C <sub>2</sub> O <sub>2</sub>		H <sub>2</sub> C <sub>2</sub> O <sub>3</sub>	
dehydrogenation	3	3'	4	4'	6	6'	7	7'
$E_a$	81.83 (76.81) <sup>b</sup>	59.36 (61.01)	67.51 (56.75)	36.11 (38.24)	57.16 (45.66)	61.37 (56.29)	51.29 (44.53)	43.42 (41.30)
$\Delta E_a$	-22.47 (-15.80) <sup>b</sup>		-31.40 (-18.51)		+4.21 (+10.63)		-7.87 (-3.23)	
dehydration	HCOOH		H <sub>2</sub> CO <sub>3</sub>		H <sub>2</sub> C <sub>2</sub> O <sub>3</sub>		H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	
	4	4''	5	5''	7	7''	8	8''
$E_a$	68.63 (63.52)	42.54 (42.80)	39.08 (33.48)	10.59 (16.86)	65.98 (59.68)	47.61 (44.90)	31.70 (35.39)	19.21 (25.09)
$\Delta E_a$	-26.09 (-20.72)		-28.49 (-16.62)		-18.37 (-14.78)		-12.49 (-10.29)	

<sup>a</sup> See Charts 1 and 2 for molecule definitions. The quantities in parentheses are the corresponding free energies. The experimental  $E_a$  values are given in footnote c.  $E_a = E(\text{TS}) - E(\text{R})$ . The total electronic energies and zero-point vibrational energies of reactant (**R**) are (-114.476483, 0.0267147) hartree for **3**, (-189.728231, 0.033987) for **4**, (-264.965060, 0.0398734) for **5**, (-277.784288, 0.0370653) for **6**, (-303.031482, 0.0435943) for **7**, and (-378.272182, 0.0489401) for **8**. <sup>b</sup> Corresponding quantities of free energies to  $E_a$  and  $\Delta E_a$ . <sup>c</sup> Experimental  $E_a$  values (all in the gas phase except the dehydration for **5**): (1) dehydrogenation: ~80.6 kcal/mol for **3**,<sup>22</sup> 62–65 kcal/mol for **4**,<sup>27</sup>  $\leq 62.9$  kcal/mol for **6**.<sup>29</sup> (2) Dehydration: 65–68 kcal/mol for **4**,<sup>27</sup> 14.6 kcal/mol in aqueous solution for **5**,<sup>16</sup> 32.8 kcal/mol for **8**.<sup>36</sup>

**Chart 2**

state (**9**). In contrast, the bonding of the leaving hydroxyl group is strongly directional. It can form a new bond only along some restricted direction approximately tetrahedral to both the cleaved C–O bond and the O–H bond (**10**). The calculated angles can be found in Figure 1a–h. In other words, the transition structure for the dehydrogenation reaction system is generally less strained than that of the dehydration reaction system for the same ring size. This idea was well documented in inorganic chemistry, where the reactivities of reductive elimination for bond formation are given in the decreasing order H–H > C–H > C–C. Their bonding energies are comparable and the relative reactivities were interpreted in terms of the favorable nondirectional bonding property of the hydrogen atom.<sup>42</sup> It is understood that there is no directionality to the bonding of a hydrogen atom for the case of the covalent bond. In the case of the hydrogen bond due to Coulombic interaction, the linear geometry is preferred.<sup>43</sup>



To demonstrate this idea qualitatively, we compare the bond order (BO) based on NAO<sup>41</sup> between the two leaving groups for the two types of reactions in the transition states for **3**–**8** in

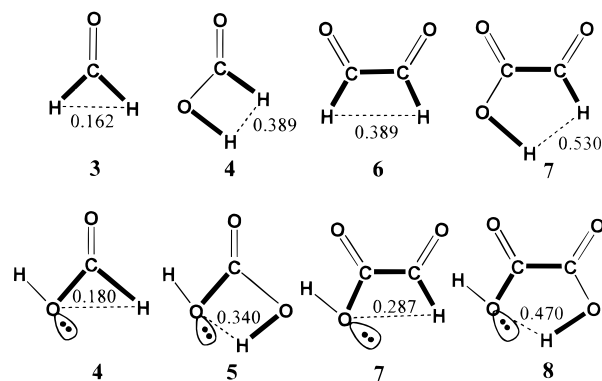
**Chart 3**

Chart 3. The BOs for the dehydrogenation reactions given in the first row have larger values than the corresponding values of the dehydration reaction of the same ring size given in the second row. The only exception is the three-membered system **3** with 0.162, which is smaller than that of **4** with 0.180.

It is understandable that the dehydrogenation of **3** is a forbidden 4-electron reaction involving two C–H bonds and the dehydration of **4** is an allowed 6-electron process involving C–H, C–O, and an in-plane lone pair on oxygen. Here we use the bold lines to indicate the active bonds to be cleaved. The BO value carries the information not only for the strain but also for the forbiddenness of the reaction. This also explains that the BO value for the dehydrogenation of **4**, a forbidden reaction, is not much greater than the value for the dehydration of **5**, an allowed reaction. For the dehydration reaction, a nonbonding electron pair is involved, which results in a disconnection in the cyclic orbital overlap. This transformation has been termed the pseudopericyclic reaction.<sup>43</sup> The reaction is allowed regardless of the number of electrons involved. Therefore, we can ignore the electron counting in the second row in Chart 3 and also the water-assisted reactions in Chart 2. All of them are considered as allowed reactions.

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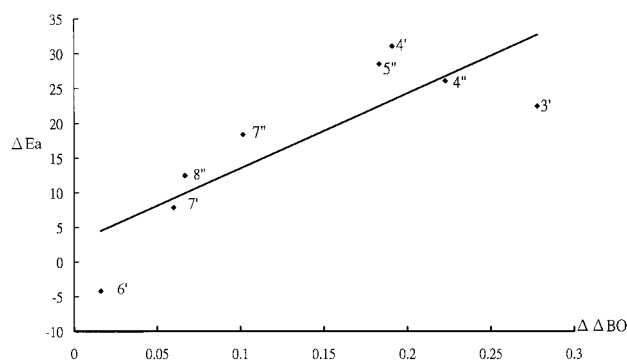
(43) Scheiner, S. *Acc. Chem. Res.* **1994**, *27*, 402.



**Table 2.** The NAO<sup>a</sup> Bond Order Difference ( $\Delta\text{BO}$ )<sup>b</sup> between **TS** and **R**, and  $\Delta\text{BO}$  Difference between Water-Assisted Reaction and Water-Free Reaction ( $\Delta\Delta\text{BO}$ ),<sup>c</sup> with Approximation ( $\Delta\Delta\text{BO}^*$ )<sup>d,e</sup>

	monocarbonyl				dicarbonyl			
	$\text{H}_2\text{CO}$		$\text{HCOOH}$		$\text{H}_2\text{C}_2\text{O}_2$		$\text{H}_2\text{C}_2\text{O}_3$	
dehydrogenation	<b>3</b>	<b>3'</b>	<b>4</b>	<b>4'</b>	<b>6</b>	<b>6'</b>	<b>7</b>	<b>7'</b>
$\Delta\text{BO}$	-0.1534	0.1243	0.0344	0.2251	-0.2111	-0.1950	0.1142	0.1739
$\Delta\Delta\text{BO}(\Delta\Delta\text{BO}^*)$	0.2777(0.3647)		0.1907(0.1912)		0.0161(0.1515)		0.0597(0.0864)	
	$\text{HCOOH}$		$\text{H}_2\text{CO}_3$		$\text{H}_2\text{C}_2\text{O}_3$		$\text{H}_2\text{C}_2\text{O}_4$	
	<b>4</b>	<b>4''</b>	<b>5</b>	<b>5''</b>	<b>7</b>	<b>7''</b>	<b>8</b>	<b>8''</b>
dehydration								
$\Delta\text{BO}$	-0.3480	-0.1254	-0.0422	0.1405	-0.4309	-0.3295	-0.0930	-0.0265
$\Delta\Delta\text{BO}(\Delta\Delta\text{BO}^*)$	0.2226(0.2241)		0.1827(0.1585)		0.1014(0.2000)		0.0665(0.0916)	

<sup>a</sup> Natural atomic orbital, see ref 41. <sup>b</sup>  $\Delta\text{BO} = \text{BO}(\text{TS}) - \text{BO}(\text{R})$ . <sup>c</sup>  $\Delta\Delta\text{BO} = \Delta\text{BO}(\text{with H}_2\text{O}) - \Delta\text{BO}(\text{without H}_2\text{O})$ . <sup>d</sup>  $\Delta\Delta\text{BO}^*$  is an approximation to  $\Delta\Delta\text{BO}$  considering only the BO between the leaving groups (H- -H) or (H- -OH) in water-free reaction and BO involved assisting water (H- -H<sub>2</sub>O- -H) or (H- -H<sub>2</sub>O- -OH) in water-assisted reaction. <sup>e</sup> See Charts 1 and 2 for molecule definitions.

**Figure 2.** The correlation between activation lowering  $\Delta E_a$  ( $E_a(\text{with H}_2\text{O}) - E_a(\text{without H}_2\text{O})$ ) given in Table 1 and the change in bond order  $\Delta\Delta\text{BO} = \Delta\text{BO}(\text{with H}_2\text{O}) - \Delta\text{BO}(\text{without H}_2\text{O})$ .  $\Delta\text{BO}$  is defined as  $\text{BO}(\text{TS}) - \text{BO}(\text{R})$ . See eqs 1 and 2, Table 2, and text. For system definitions, see Chart 1, and 2.

Since the sum of the bond order (BO) around the ring in the transition structure can serve as a measurement of the reaction forbiddenness and ring strain, we have carried out bond order calculations between the nearest neighbor atoms around the reaction ring, including the inactive side chains such as OH groups and carbonyl groups. We first considered the change in bond order between the transition structure and the reactant ( $\Delta\text{BO}$ ):

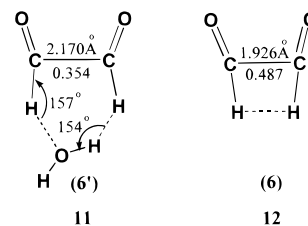
$$\Delta\text{BO} = \text{BO}(\text{TS}) - \text{BO}(\text{R}) \quad (1)$$

$$\Delta\Delta\text{BO} = \Delta\text{BO}(\text{with H}_2\text{O}) - \Delta\text{BO}(\text{without H}_2\text{O}) \quad (2)$$

The quantity  $\Delta\Delta\text{BO}$  (see Table 2) is defined as the difference between the  $\Delta\text{BO}$  value for the reaction with  $\text{H}_2\text{O}$  and that without  $\text{H}_2\text{O}$ . The double subtraction eliminates the necessity to account for the different numbers of atoms involved in the water-free and water-assisted system.  $\Delta\Delta\text{BO}$  is an indication of the improvement in reaction forbiddenness and strain relief. We found a qualitative correlation between  $\Delta E_a$  values and  $\Delta\Delta\text{BO}$  values as shown in Figure 2. We do not expect a close correlation between  $\Delta E_a$  and  $\Delta\Delta\text{BO}$  since  $E_a$  involves energy matrix elements such as  $H_{ij}$  and BO involves overlap matrix elements such as  $S_{ij}$ . Their equivalence needs a weighting factor of atomic orbital energy such as in the Hückel approximation  $H_{ij} = S_{ij}(H_{ii} + H_{jj})/2$ . The light hydrogen atom and the heavy oxygen and carbon atoms should associate with rather different weighting factors.

To examine the local interaction contribution from the assisting water molecule, we also study the quantity  $\Delta\Delta\text{BO}^*$ , which includes only the BO values between the leaving groups

with the assisting  $\text{H}_2\text{O}$  such as (H- -H<sub>2</sub>O- -H) or (H- -H<sub>2</sub>O- -OH) plus the BO values within the  $\text{H}_2\text{O}$  molecule itself. For the water-free reaction, the  $\Delta\Delta\text{BO}^*$  includes only the BO between the two leaving group, such as (H- -H) in dehydrogenation and (H- -OH) for the dehydration. There is a qualitative correlation between  $\Delta\Delta\text{BO}$  and  $\Delta\Delta\text{BO}^*$  except for the systems **3'** and **6'** (see Chart 2). Some reasonable correlations between  $\Delta E_a$  and  $\Delta\Delta\text{BO}$ , and between  $\Delta\Delta\text{BO}$  and  $\Delta\Delta\text{BO}^*$ , imply that the improvements in reaction forbiddenness and strain relief are due to local interactions involving the assisting  $\text{H}_2\text{O}$ . The poor correlation between  $\Delta\Delta\text{BO}$  and  $\Delta\Delta\text{BO}^*$  for **3'** may be due to a switch from forbidden to allowed reaction contributed by all the bonds in the ring, not simply the local interactions between the leaving hydrogens and the assisting  $\text{H}_2\text{O}$ . When we examine the transition state of **6'** closely, we find the C-C bond stretches to 2.170 Å and BO reduces to 0.354 from the values (1.926 Å, 0.487) for the transition



structure for **6** (see structure **11** and **12**). If we add the reduction in BO contribution of 0.133 from the C-C bond to the  $\Delta\Delta\text{BO}^*$  value, then it agrees well with the  $\Delta\Delta\text{BO}$  values. Therefore, the water-assisted effect in **6'** is nonlocal. We interpret this to mean that to satisfy the stringent geometry requirement for the assisting  $\text{H}_2\text{O}$  molecule, the weak C-C bond has to stretch. Therefore, the participation of water does not reduce, but rather induce the strain. We also find the two leaving groups A and B in the water-assisted reaction are arranged with a nearly linear geometry in the transition state for C-A-O( $\text{H}_2\text{O}$ ) and ( $\text{H}_2\text{O}$ )O-H-B. For example, the two angles are 157° and 154°, shown in structure **11** for **6'**. In all cases it ranges from 140° to 170° as shown in Chart 2. Thus there is a considerable modification in the reaction coordinate. The nearly linear geometry here means that both C-H stretching toward oxygen ( $\text{H}_2\text{O}$ ) and O-H ( $\text{H}_2\text{O}$ ) stretching toward H-H formation (structure **11**) are the modified new reaction coordinates, which are in contrast to the original C-H bending motion in the water-free reaction (structure **12**).

A summary of our interpretation on the contributions to  $\Delta E_a$  can be given in Chart 4. We assign the water-assisted dehydrogenation reaction as an ineffective strain relief process for

**Table 3.** The Bond Distance Difference ( $\Delta R_1$ ,  $\Delta R_2$ ) between the Transition State and the Reactant for the Two Leaving Groups (See Text for Details)<sup>a</sup>

	water-free			water-assisted				
	$R_1(\text{TS})$ $R_1(\mathbf{R})$	$\Delta R_1$	$R_2(\text{TS})$ $R_2(\mathbf{R})$	$\Delta R_2$	$R_1(\text{TS})$ $R_1(\mathbf{R})$	$\Delta R_1$	$R_2(\text{TS})$ $R_2(\mathbf{R})$	$\Delta R_2$
dehydrogenation								
H <sub>2</sub> CO ( <b>3</b> )	1.673	<b>0.562</b>	1.092	-0.017	1.606	<b>0.495</b>	1.412	<b>0.304</b>
	1.110		1.110		1.110		1.107	
HCOOH ( <b>4</b> )	1.447	<b>0.339</b>	1.307	<b>0.339</b>	1.413	<b>0.304</b>	1.494	<b>0.509</b>
	1.107		0.968		1.108		0.984	
H <sub>2</sub> C <sub>2</sub> O <sub>2</sub> ( <b>6</b> )	1.437	<b>0.324</b>	1.437	<b>0.324</b>	1.452	<b>0.343</b>	1.463	<b>0.355</b>
	1.112		1.112		1.108		1.108	
H <sub>2</sub> C <sub>2</sub> O <sub>3</sub> ( <b>7</b> )	1.608	<b>0.484</b>	1.371	<b>0.401</b>	1.472	<b>0.361</b>	1.564	<b>0.580</b>
	1.116		0.969		1.111		0.984	
dehydration								
HCOOH ( <b>4</b> )	1.833	<b>0.485</b>	1.161	<b>0.061</b>	1.784	<b>0.425</b>	1.387	<b>0.289</b>
	1.347		1.100		1.358		1.097	
H <sub>2</sub> CO <sub>3</sub> ( <b>5</b> )	1.669	<b>0.309</b>	1.244	<b>0.275</b>	1.594	<b>0.213</b>	1.411	<b>0.419</b>
	1.360		0.969		1.381		0.992	
H <sub>2</sub> C <sub>2</sub> O <sub>3</sub> ( <b>7</b> )	1.734	<b>0.383</b>	1.280	<b>0.172</b>	1.632	<b>0.270</b>	1.476	<b>0.371</b>
	1.351		1.107		1.362		1.105	
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ( <b>8</b> )	1.793	<b>0.433</b>	1.397	<b>0.426</b>	1.732	<b>0.363</b>	1.575	<b>0.583</b>
	1.360		0.971		1.369		0.992	

<sup>a</sup> The values are given for both water-free and water-assisted reactions.

both monocarbonyl and dicarbonyl systems. The ineffectiveness here is understood only in a sense relative to the dehydration process for the same ring size, for example, the rings of **7** → **7'** and **8** → **8''** (see Chart 2) are both increased from five-membered to seven-membered. Because the bonding of hydrogen is less directional, the assistance from the water molecule is less helpful for **7** → **7'** than for **8** → **8''**.

#### Chart 4

	mono-carbonyl	di-carbonyl
dehydrogenation	<b>3</b> → <b>3'</b> <b>4</b> → <b>4'</b>	<b>6</b> → <b>6'</b> <b>7</b> → <b>7'</b>
	forbidden to allowed	allowed to allowed
	ineffective strain relief	ineffective strain relief
dehydration	<b>4</b> → <b>4''</b> <b>5</b> → <b>5''</b>	<b>7</b> → <b>7''</b> <b>8</b> → <b>8''</b>
	allowed to allowed	allowed to allowed
	effective strain relief	effective strain relief

Chart 4 explains qualitatively that **6** → **6'** and **7** → **7'** in the upper right block for the dehydrogenation of dicarbonyl systems have the lowest  $\Delta E_a$  value. It also explains that the other three blocks have larger values more or less similar to each other. Another interesting observation is that the pairs (**3'**, **6'**), (**4'**, **7'**), (**4''**, **7''**), and (**5''**, **8''**) have similar  $E_a$  values as shown in Table 1. Each pair, as (mono-, di-) carbonyl have the ring size ( $n$ ,  $n + 1$ ), differ by only one carbonyl group. All of them are allowed reactions (pseudopericyclic reactions). Some convergence of  $E_a$  values is evident with respect to the ring size  $n$  to  $n + 1$  with  $n \geq 5$ . The existence of such a boundary condition is reasonable and anticipated and should dictate the  $\Delta E_a$  values we observed.

#### (III) Asynchronicity between the Two Leaving Groups.

We also studied a third effect in the water-assisted reactions besides the strain relief and electronic effects, namely, the asynchronicity<sup>45,46</sup> of the two leaving groups, H and OH (or a

second H for the dehydrogenation process). Our discussion has been motivated by the work of Nguyen et al.,<sup>17</sup> who studied the transition structures for the addition reactions of CO<sub>2</sub> with (H<sub>2</sub>O)<sub>*n*</sub>,  $n = 1, 2, 3$ . For the dehydration reaction, we use  $\Delta R_1$  to denote the difference in the C–OH bond length between the transition state and the reactant and  $\Delta R_2$  for the C–H bond (the CO–H bond for **5** and **8**).

dehydration reaction:

$$\Delta R_1 = R_{\text{C-OH}}(\text{TS}) - R_{\text{C-OH}}(\mathbf{R}) \quad (3)$$

$$\Delta R_2 = R_{\text{C-H}}(\text{TS}) - R_{\text{C-H}}(\mathbf{R}) \quad (4)$$

For dehydrogenation reaction,  $\Delta R_1$  refers to the C–H bond and  $\Delta R_2$  refers to the CO–H bond or the second C–H bond for compound **3** and **6**.

dehydrogenation reaction:

$$\Delta R_1 = R_{\text{C-H}}(\text{TS}) - R_{\text{C-H}}(\mathbf{R}) \quad (5)$$

$$\Delta R_2 = R_{\text{CO-H}}(\text{TS}) - R_{\text{CO-H}}(\mathbf{R}) \quad (6)$$

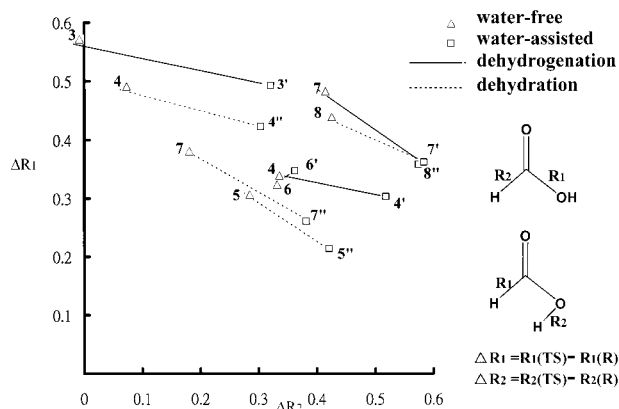
For both dehydration and dehydrogenation,  $\Delta R_1$  is consistently defined for the negatively charged leaving group, as well as  $\Delta R_2$  for the positively charged one. The quantities  $\Delta R_i$  defined here are similar in spirit to the quantities  $\delta \text{Bi}$ , a relative variation of bond index used by Moyano et al. in studying the asynchronicity between the two cleaved bonds in the thermolysis of 2-oxetanes.<sup>45</sup>

Our interest is to examine the changes in  $\Delta R_1$  and  $\Delta R_2$  in the water-assisted reaction as compared to the water-free reaction, shown in Table 3. We find a substantial increase of  $\Delta R_2$  and a slight decrease of  $\Delta R_1$  caused by the additional H<sub>2</sub>O. Molecule **3** is interesting in that  $R_2$  is shorter in the transition state than in the reactant. It is a forbidden reaction with a zwitterion-like transition structure. With hydride leaving and protonated carbon monoxide left behind, there is a strengthening in the C–H bond. Figure 3 gives the essential information of Table 3, which shows the lines connecting the point ( $\Delta R_1$ ,  $\Delta R_2$ ) on the left for the water-free reaction with the corresponding point on the right for the water-assisted reaction. The lines all have about the same slope. The only exception is molecule **6**,

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**Figure 3.** The changes of ( $\Delta R_1$ ,  $\Delta R_2$ ) from water-free reaction (left end of the line) toward water-assisted reaction (right end of the line): (—) for dehydrogenation reaction and (---) for dehydration. See text or Table 3 for the definitions and values of ( $\Delta R_1$ ,  $\Delta R_2$ ). See Charts 1 and 2 for system definitions.

for which  $\text{H}_2\text{O}$  participation hardly modifies the bond lengths of the reaction coordinate at all despite a substantial change in structure involving bond angles as discussed previously. We can compare our DFT results for **5** ( $\text{H}_2\text{CO}_3$ ) with the MP2 result of Nguyen et al.,<sup>17</sup> the only system with available data. Our ( $\Delta R_1$ ,  $\Delta R_2$ ) for the water-free and water-assisted reactions, (0.309, 0.275) and (0.213, 0.419), respectively, compared well with Nguyen's corresponding values (0.308, 0.265) and (0.212, 0.414), in better than 1% agreement. The substantial shift in  $\Delta R_2$  indicates that in the water-assisted reaction, the H atom of the C–H bond is considerably shifted toward  $\text{H}_2\text{O}$  to form  $\text{H}_3\text{O}^+$  in the transition state. Simultaneously, the OH stretching is reduced because of easier access to a proton from the  $\text{H}_3\text{O}$  group intervening between the two leaving groups. The Mulliken charges<sup>47</sup> for transition states in Table 4 give a consistent picture: the leaving H atom in the water-free reaction has a smaller positive charge than the  $\text{H}_3\text{O}$  group in the water-assisted reaction. The changes are not drastic, ranging from +0.36 for **6** to +0.06 for **3**, about +0.15 on average. Qualitatively speaking, one observes a shift in character from hydrogen-like transfer with smaller positive charge on the H atom in the water-free reaction toward proton-like transfer with larger positive charge on  $\text{H}_3\text{O}$  in the water-assisted reaction. Ha<sup>18</sup> mentioned that in the presence of an additional  $\text{H}_2\text{O}$ , a  $\text{H}_2\text{O}$  molecule can reduce its heterolytic bond dissociation energy effectively, from  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$  with 420 kcal/mol to  $(\text{H}_2\text{O})_2 \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$  with 240 kcal/mol. Therefore, in the water-assisted reaction, the two leaving groups become more asynchronous in comparison with the water-free reaction.

Since the transition state of the water-assisted reaction has a significantly larger charge separation than that in the water-

**Table 4.** Mulliken Charge<sup>a</sup> on H ( $\rho_{\text{H}}$ ) of Water-Free Reaction and on the  $\text{H}_3\text{O}$  Group ( $\rho_{\text{H}_3\text{O}}$ ) of Water-Assisted Reaction for Transition Structure

	monocarbonyl		di-carbonyl	
	$\text{H}_2\text{CO}$ (3)	$\text{HCOOH}$ (4)	$\text{H}_2\text{C}_2\text{O}_2$ (6)	$\text{H}_2\text{C}_2\text{O}_3$ (7)
dehydrogenation				
$\rho_{\text{H}}$	0.2799	0.2929	0.0149	0.2347
$\rho_{\text{H}_3\text{O}}$	0.3417	0.4706	0.3717	0.4262
dehydration	$\text{HCOOH}$ (4)	$\text{H}_2\text{CO}_3$ (5)	$\text{H}_2\text{C}_2\text{O}_3$ (7)	$\text{H}_2\text{C}_2\text{O}_4$ (8)
$\rho_{\text{H}}$	0.3254	0.4084	0.3487	0.4112
$\rho_{\text{H}_3\text{O}}$	0.3906	0.5593	0.4625	0.4913

<sup>a</sup> See ref 47.

free reaction, one expects the former has a larger solvent electrostatic stabilization effect. Nguyen found that water-free and water-assisted reactions for the  $\text{CO}_2$  hydration have their  $E_a$  lowering of 0.71 and 4.30 kcal/mol, respectively, in the SCRFP type solvent model study.

## Conclusion

In the water-assisted reaction, the water has an obvious effect of geometric strain relief. However, it is useful to distinguish between dehydrogenation and dehydration reactions. Since the bonding of the hydrogen atom is less directional, the transition state of the dehydrogenation is less strained and thus receives a less strain relief effect than that in the dehydration reaction with the same ring size. The water-assisted reaction also has an important electronic effect due to the participation of an additional electron pair from the O–H bond and a lone pair. This effect can switch the original forbidden reaction to an allowed pseudopericyclic reaction. The reactions of the dicarbonyl series studied here are allowed reactions and the participation of  $\text{H}_2\text{O}$  is less helpful, especially for the dehydrogenation reaction. The water-assisted reaction also amplifies the asynchronicity between the two leaving groups via the intermediate formation of  $\text{H}_3\text{O}^+$  in a qualitative sense. This is consistent with an increase of positive charge from the leaving H atom in the water-free reaction to the  $\text{H}_3\text{O}$  group in the water-assisted reaction.

**Acknowledgment.** We are grateful to a referee for calling our attention to the pseudopericyclic reaction, deficiencies in the Mulliken charge, and the novel transition structure for **3**. We would like to thank the National Center for High-Performance Computing of Taiwan and the Computing Center at Tsing Hua University for generous allocation of computing time. The National Science Council of Taiwan is also acknowledged for their financial support.

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(47) Mulliken charge is known to have some deficiencies as pointed out by a referee and we use it only for comparison purposes. (a) Williams, D. E. In *Reviews in Computational Chemistry*; Boyd, D., Lipkowitz, K., Eds.; Wiley-Interscience: New York, 1991; p 219. (b) Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894. (c) Sokalski, W. A.; Keller, D. A.; Ornstein, R. L.; Rein, R. J. *J. Comput. Chem.* **1993**, *14*, 970.

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