negie-Mellon University and Lila Gierasch of the University of Delaware. We thank Mr. Michael M. Kornbluth for his assistance in the data analysis and management, which was mainly performed using the PROPHET computer network developed and supported by the Division of Research Resources, NIH. We also appreciate the diligent efforts of Mr. William H. Craig for maintaining our WH-90 and for his innovative electronic wizardry in building the high-power homodecoupler described herein. Finally, we thank Miss Alice L. Reid for her data on compound **10B**.[23]

Registry No. 1A, 3306-69-2; **1B**, 88842-37-9; **2A**, 88842-36-8; **2B**, 88842-38-0; **3A**, 37488-26-9; **3B**, 88842-39-1; **4A**, 25772-44-5; **4B**, 88842-40-4; **5A**, 105-60-2; **5B**, 23649-75-4; **6A**, 616-45-5; **6B**, 23649-65-2; **7A**, 675-20-7; **7B**, 23649-68-5; **8A**, 2425-74-3; **8B**, 88842-41-5; **9A**, 20198-92-9; **9B**, 52072-73-8; **10A**, 1906-82-7; **10B**, 88842-42-6; camphene, 79-92-5; chlorosulfonyl isocyanate, 1189-71-5; α-pinene, 80-56-8; cycloheptatriene, 544-25-2; CF_3OF, 373-91-1.

Molecular Orbital Study on the Hydrolysis of Ketene by Water Dimer: β-Carbon vs. Oxygen Protonation?

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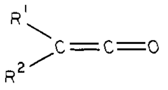
Abstract: The detailed reaction pathway for the hydration of ketene ($CH_2{=}C{=}O$) by water dimer has been investigated by ab initio methods using STO-3G and 4-31G basis sets. Two transition states for the reaction have been compared (using the gradient method to determine saddle points on the energy surface) involving addition of water across the C=C and C=O bonds. The latter process (to yield a ketene hydrate $CH_2{=}C(OH)_2$ initially) is markedly favored (activation barrier 13 kcal mol^{-1}), compared to direct formation of acetic acid (24 kcal mol^{-1}, also in 4-31G). This contrasts with preequilibrium proton transfer to the carbon of the ketene, which gives a more stable species (CH_3CO^+) than does proton transfer to oxygen (to give CH_2COH^+). These findings are compared with experimental results and the intermediacy of reactive ketene hydrates and cyclic mechanisms commented on.

Ketenes (**1**), as members of the cumulene family, undergo a wide range of additions with nucleophilic reagents and cycloadditions to unsaturated substrates; they also serve as intermediates for acylation reactions.[1] It is well-known that in a strongly acidic mixture, the rapid protonation of ketenes occurs at the terminal carbon atom (C_β) rather than at the oxygen atom.[2] The energy difference between the C_β-protonated (**2**) and oxygen-protonated (**3**) isomers was calculated to be 37 kcal/mol at SCF level with double-ζ basis set[3] in favor of C_β-protonated ketene **2**.



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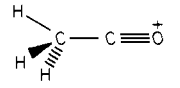

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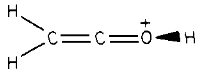

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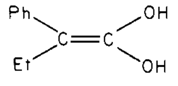
In the spontaneous reaction of ketenes with nucleophilic reagents such as alcohols, amines, and carboxylic acids, nucleophilic attack at the C_α atom was generally accompanied by a proton transfer to the C_β atom.[4] In the same way, the hydrolysis of various ketenes classically leads to the formation of carboxylic acids.[5] These additions were assumed from kinetic studies to occur via cyclic transition states that involve the C=C bond of ketenes.[6]

Bothe and co-workers[7] recently reported an experimental study of the rate and mechanism of hydration of the unsubstituted ketene ($CH_2{=}C{=}O$). In aqueous solution (pH 4.4–9.85), the observed rate constants for hydrolysis were shown to be independent of pH but approximatively proportional to the water concentration. A solvent kinetic isotope effect of $k_{H_2O}/k_{D_2O} = 1.9$ has been measured. These authors also reported an activation enthalpy of 10.3 kcal/mol and an activation entropy of −16 eu. Acetic acid as its dissociated form is observed as product. It is concluded that the water is acting as nucleophilic reagent rather than the proton (H^+ or H_3O^+) donor in the first step of the hydrolysis. However, the question remains unanswered as to whether the acetic acid was produced directly from this first step or only in a subsequent step, that is, whether the hydrolysis has occurred by C_β protonation or by oxygen protonation.

More recently, we have carried out the hydration of phenylethylketene in an acetonitrile/water mixture with 1–5% of water. From our kinetic measurements[8] we cannot rule out the participation of the 1,1-ethylenediol **4** as an intermediate in the hydrolysis of phenylethylketene (the final product is the substituted acetic acid **5**). In solution, the transformation of enol **4** to ketone **5** should be a fast process.



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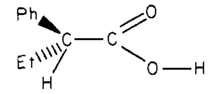

5

We have also observed a strongly negative activation entropy of −50 eu for the formation of **5**, which is much larger than the value of −16 eu previously reported for CH_2CO.[7] However, this entropy value, which suggests a highly ordered activated complex, appears to be consistent with the observation of Satchell et al.[5,6] According to these authors, the spontaneous hydration of ketenes with water is autocatalytic, the cyclic transition states containing, besides the ketene molecule, two water molecules. These latter react as a dimer rather than two monomers. Moreover, there is

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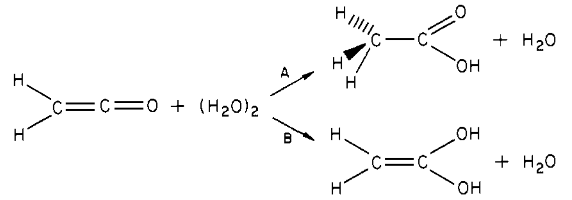
no evidence for a path involving only a single water molecule.

Recently, by means of ab initio calculations, we have shown that the preferred reaction pathway in the hydration of ketene imine ($CH_2=C=NH$)[9] and carbon dioxide ($O=C=O$)[10] is with water dimer through a preassociation mechanism. The same theoretical observation was also found for the addition of water to formaldehyde.[11] Thus, there are already precedents for the hydrolysis of a double bond by a dimer of water (in which the second water molecule acts as a catalyst).

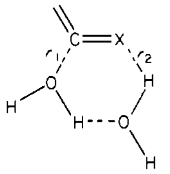
In this present work, we examine the site of proton addition—C_β vs. O atom—during the neutral hydrolysis of unsubstituted ketene by water dimer (using reactions A and B). Some comparisons with hydration of other members of the cumulene family are also presented.



Experimental Section

Details of Calculations. The energy calculations were carried out by the ab initio method of Roothaan,[12] and the classical model of the supermolecule has been adopted. The minimal STO-3G basis set[13] was used to optimize the geometries of stationary points on the energy supersurfaces. For comparing the relative energies with results previously presented for other additions, we recalculate the single-point energies with the split-valence 4-31G basis set[14] using the optimized STO-3G geometries.

The optimally conditioned minimization technique[15] was employed for searching the minima or minimizing the energies. For locating the transition states, we have used the classical distinguished-coordinate methods.[16,17] In order to force the approach of $(H_2O)_2$ to the $C=C$ and $C=O$ double bonds of ketene, the more rigorous direct location method[18] cannot be applied here. First, we have chosen two geometrical parameters, r_1 and r_2, as shown in **6**, as independent variables. The other structural parameters were then optimized by minimizing the total energy. It is well established that in this method a discontinuity might be created in the supersurface[19] and some of the remaining geometric parameters might also intervene in the reaction coordinate.



6, X = O, CH_2

Generally, one or more parameters that are greatly modified during the reaction should be considered.[20] However, such a procedure requires an enormous amount of geometry optimization. In order to ensure that true transition-state structures are obtained, several points in the saddle region (as located in the (r_1,r_2) two-dimensional surface of each reaction) were reoptimized by the VA05AD method[21] in which the Hessian matrices are computed by gradient differences. The order of critical points can thus be checked by eigenvalues of the Hessian matrix. Carefully done, this approach is comparable with other strategies[19,21-23] in locating transition states and avoids the danger of the energy surface discontinuity problem.[19] Note that all optimizations were terminated when the gradient length $g = (\sum_i^n(\delta E/\delta qi)^2/n)^{1/2}$ was reduced below 5×10^{-4} mdyn. Finally, the charge centroids of the localized orbitals were obtained by means of the Foster–Boys method[24] using the Boyloc program.[25] All calculation procedures are implemented in the Monstergauss program.[26]

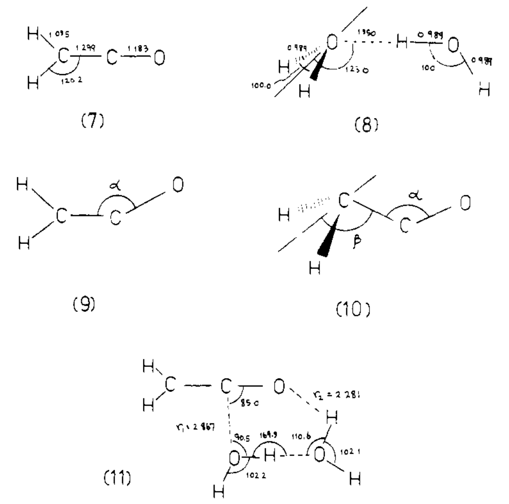


Figure 1. Optimized geometries (STO-3G) of reactants **7** and **8** and complex **11**. The two basic deformation modes of the ketene are given in **9** and **10**.

Table I. Calculated (STO-3G) Energies for Ketene in Two Deformed Geometries (in au)

α, deg	9[a]	10[a,d]
170[b]	−149.72435 (1.11)[c]	−149.72408 (1.27)
160	−149.71728 (5.54)	−149.71790 (5.15)
150	−149.70691 (12.67)	−149.70716 (11.89)

[a] See Figure 1. [b] α is fixed; all remaining parameters are optimized. [c] Relative energies in kcal/mol with respect to the undeformed ketene (−149.72611 au). [d] The optimized values for β angles in 10 are respectively 173.4°, 166.7°, and 160.1°.

Results and Discussion

Deformation of the Ketene. The molecular and electronic structures of ketene (**7**) and water dimer (**8**) have been extensively studied previously.[1,27,28] We now report on the nuclear deformation of the ketene. For this molecule, there are two principal modes of deformation: the bending in the plane (**9**)) (C_1) and the bending out the plane (**10**) (C_s) of the α = CCO angle (see Figure 1).

The energies corresponding to optimized geometries with three fixed values for the angle α of 170°, 160°, and 150° in both modes are collected in Table I. It is interesting to note that both deformations almost require an equivalent energy. For small values of α, the bending out the plane (**8**) is slightly favored. Unlike the ketene imine ($CH_2=C=NH$) where the cis-deformation (retaining the two groups CH_2 and NH on the same side of the $C=C$) is preferred, the trans deformation is more favorable in the ketene molecule. This trans deformation has also been observed in the diazomethane molecule[29] and fulminic acid.[20] It

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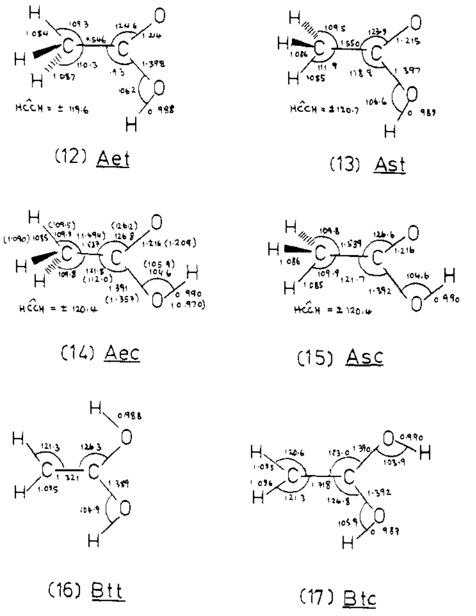


(12) Aet (13) Ast (14) Aec (15) Asc (16) Btt (17) Btc

Figure 2. Optimized geometries (STO-3G) of different conformations of acetic acid (A) and 1,1-ethenediol (B); s = staggered, e = eclipsed, c = s-cis and t = s-trans. Values in parentheseses are experimental.[30]

seems that in the ketene imine, the configuration with respect to the C=N double bond determines the mode of deformation of this molecule. The deformation of ketene (12 kcal/mol) for closing the angle α by 30°) requires more energy than that of ketene imine (8 kcal/mol for the same closure).

Molecular Complexes between CH_2=C=O and $(H_2O)_2$. The most stable complex has structure **11** (see Figure 1) with a formation energy of −1.5 kcal/mol (STO-3G) relative to the CH_2CO + $(H_2O)_2$ system. This is a particularly small value that is probably due to an artifact of a minimal basis set. Indeed, when we previously computed the complex between CO_2 and $(H_2O)_2$ with STO-3G, the formation energy was also calculated to be about −2 kcal/mol, which is significantly smaller than the values of −13.2 and −10.3 kcal/mol, respectively, obtained with 3-21G[10] and 4-31G basis sets.[29] The optimized values of 2.374/1.987 Å obtained with 3-21G for the r_1/r_2 distances[10] are much shorter than the 2.867/2.281 Å values with STO-3G in **11**. We have previously shown that the complexes of type **11** play an important role in the hydration of the CO_2 molecule.[10]

Geometry of Product. In Figure 2 are given the geometries of different conformations of the products formed from two reactions (reactions A and B, viz. acetic acid (CH_3COOH, A) and 1,1-ethylenediol (CH_2=C$(OH)_2$, B). The acetic acid A can exist in staggered (s) and eclipsed (e) conformation for the methyl group and in s-cis (e) and s-trans (t) relative to the C–O single bond. The ethylenediol possesses two planar conformers, s-trans–s-trans (Btt) and s-trans–s-cis (Btc), with respect to the two C–O bonds. s-cis–s-cis is found to be a saddle point in the energy surface. The total and relative energies of various structures are recorded in Table II. In agreement with experimental data[30] the conformer (**14**) Aec is the most stable for acetic acid. However, in comparison with the microwave geometry of **14**,[30] we note that the calculations (STO-3G) overestimate the C–C and C–O bond lengths (0.04 Å) and especially the CCO bond angle (9.8°). The energy difference between the staggered and eclipsed conformers of acetic acid is small (<1 kcal/mol), while that between s-cis and s-trans is relatively larger ($\simeq$5 kcal/mol) in favor of the s-cis forms.

Table II. Total (au) and Relative (kcal/mol) Energies of Isolated Molecules

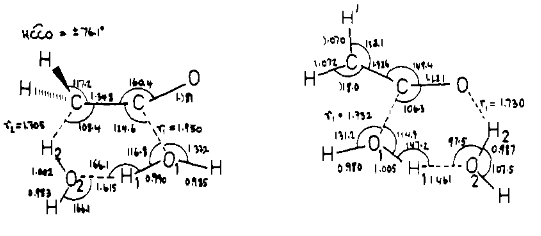
molecule[a]	STO-3G// STO-3G	ΔE- (STO-3G)[b]	4-31G// STO-3G
7	−149.72610		−151.49418
8[c]	−149.94117		−151.81957
12	−224.80206	5.1	
13	−224.80011	6.3	
14	−224.81020	0.0	
15	−224.80928	0.6	−227.46322
16	−224.76281	29.7	
17	−224.76555	28.0	−227.41830

[a] See Figures 1 and 2 for the numbering of molecules. [b] Relative energies with respect to acetic acid **14**. [c] The total energies of water monomer (H_2O) are −74.96590 and −75.90333 au in STO-3G and 4-31G basis set, respectively.

Table III. Moments of Inertia (in amu Å^2) and Rotational Constants (in MHz) Calculated with STO-3G Geometries for the Most Stable Conformer of Acetic Acid **14** and Two Conformers of Ethylenediol

constant	14, Aec[a]	16, Btt	17, Btc
Ia	45.77 (44.58)	48.99	47.67
Ib	55.75 (53.32)	49.01	50.20
Ic	98.40 (94.91)	97.99	97.88
A	11041.36 (11335.42)	1016.04	10600.99
B	9062.84 (9478.60)	10312.35	10067.86
C	5135.84 (5324.91)	5157.10	5163.77

[a] Experimental values[30] are in parentheses.



(18) (19)

Figure 3. Optimized geometries (STO-3G) for the two transition states for the reaction of CH_2CO and $(H_2O)_2$ leading to CH_3CO_2H + H_2O (**18**) and CH_2=C$(OH)_2$ + H_2O (**19**).

In contrast to the carbonic acid (0=C$(OH)_2$ where the tt conformer is the most stable,[10] the most stable conformer of the diol is tc. That is due no doubt to the interaction between the hydrogen atoms in the tt form. The diol **17** Btc lies 28 kcal/mol above the acetic acid Aec **14**. This energy difference is larger than that calculated for the vinylalcohol–acetaldehyde isomers (18.4 kcal/mol in STO-3G).[31]

In Table III we have reported the moments of inertia and rotational constants of acetic acid **14** and two conformers of the ethylenediol using optimized geometries.

Transition States. In Figure 3 we have reported the optimized geometries of two transition states. The first (**18**) connects the ketene + water dimer with acetic acid Asc (**15**) + H_2O (reaction A) and the second (**19**) with ethylenediol Btc (**17**) + H_2O (reaction B).

It is worth noting some important nuclear motions: the bending of the ketene and water dimer and the reduction of the intermolecular OH distance in the dimer. No elongation of intramolecular bond lengths has been observed. Before the supermolecule reaches structure **18** (r_1 and r_2 > 2.5 Å), the ketene molecule bends following the trans deformation (**10**), its easiest mode of deformation out of the plane.

At $r_2 \simeq 2$ Å, the methylene group (CH_2) begins to lie on the same side as the oxygen atom. It is obvious that only the cis configuration of the ketene allows the proton transfer from the water dimer directly toward the C_β atom. In some ways structure **18** is comparable to the transition states of the CH_2=C=NH

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Table IV. Total (au) and Relative (kcal/mol) Energies for Reactions of $CH_2CO + (H_2O)_2$

system[a]	STO-3G// STO-3G	4-31G// STO-3G
$CH_2 + (H_2O)_2$	−299.66727	−303.31375
18 (reaction A)‡	−299.62788	−303.27614
19 (reaction B)‡	−299.65505	−303.30717
$CH_3COOH + H_2O$ (reaction A)	−299.77518	−303.36655
$CH_2{=}C(OH)_2 + H_2O$ (reaction **B**)	−299.73145	−303.32163
activation barrier[b]		
reaction A	24.7	23.6
reaction B	7.7	4.1
heat of reaction[b]		
reaction A	−67.7	−33.1
reaction B	−40.3	−4.9

[a] See Table II for energies of isolated molecules. [b] Relative energies with respect to the $CH_2CO + (H_2O)_2$ system.

+ $(H_2O)_2$ supersystem, as previously reported.[9] The r_1 distances are close (1.95/1.93 Å) in both cases, but the r_2 distances are very different (1.705/2.376 Å).

We consider now transition state **19**. The ketene deformation that occurs here is in the molecular plane as in **9**. This fact leads to the planar conformations of ethylenediol. This transition state **19** is more compact than **18**: the CCO angle is more closed (by 11°) and the intermolecular distances such as r_1 = 1.732 Å, r_2 = 1.730 Å, and OH = 1.461 Å are all shorter than those corresponding to **18**. The r_1/r_2 values are, however, similar to those calculated in $CO_2 + (H_2O)_2$ (1.650/1.555 Å with the 3-21G basis set).[10]

After the transition states the products are formed by two simultaneous proton-transfer movements: H_1 moves toward O_2 and H_2 toward C_β or O (see Figure 3). For smaller values of r_1 and r_2, the H_1O_2H molecule forms molecular complexes of linear structure at the O_1 atom in both cases.

In Table IV are given the energies calculated by using STO-3G and 4-31G basis sets. In previous work on the addition of $CH_2{=}C{=}NH + H_2O$, we have found that the polarization effect only increased the activation barrier by ≃3 kcal/mol. Recently, Oie et al.[23] reported an extensive theoretical study on the reaction between ammonia (NH_3) and formic acid (HCOOH), which is the same type of reaction as those considered in the present study, namely nucleophilic addition to a double bond (C=O) followed by a proton transfer toward a β-atom. This study, which included a detailed analysis of the correlation and polarization effects, emphasized that correlation and polarization effects in transition-state energies act in opposite directions. This means that results from single-point energies with split valence basis sets are consistent with the results obtained from higher level calculations such as MP4/6-31G**. The authors[23] recommended the use of a split valence basis set with STO-3G geometries for the large systems.

We can now compare the predicted thermodynamic parameters (4-31G basis set) of the ketene hydration with the corresponding values for the hydration of ketene imine and carbon dioxide.[10] For the latter we have performed some additional calculations in a 4-31G basis set.[29] From Table IV, we note that both basis sets gave quite similar values for the energy differences between the acid form and the diol form and for activation barriers, but the 4-31G significantly destabilized the products.

The heat of reaction of −4.9 kcal/mol for reaction **B** leading to diol is comparable to that of ≃−2 kcal/mol obtained (with the same basis set) for the $CO_2 + (H_2O)_2$ addition.[29] If we consider now the activation barrier and the heat of reaction of reaction **B** with respect to the molecular complex **11**, which lies (in the 4-31G basis set) about 9 kcal/mol below the $CH_2CO–(H_2O)_2$ system, reaction **B** becomes slightly endothermic (≃4 kcal/mol) and the activation barrier increases to ≃13 kcal/mol. This barrier is reasonably close to the value of 12 kcal/mol in the hydration of CO_2 calculated from the complex.[29]

In the same way, the predicted activation barrier of 23.6 kcal/mol and the heat of reaction of −33.1 kcal/mol for reaction A leading to acetic acid are also similar to the corresponding values of 22 and −36.4 kcal/mol in the addition of $(H_2O)_2$ to the C=C bond in $CH_2{=}C{=}NH$.[9]

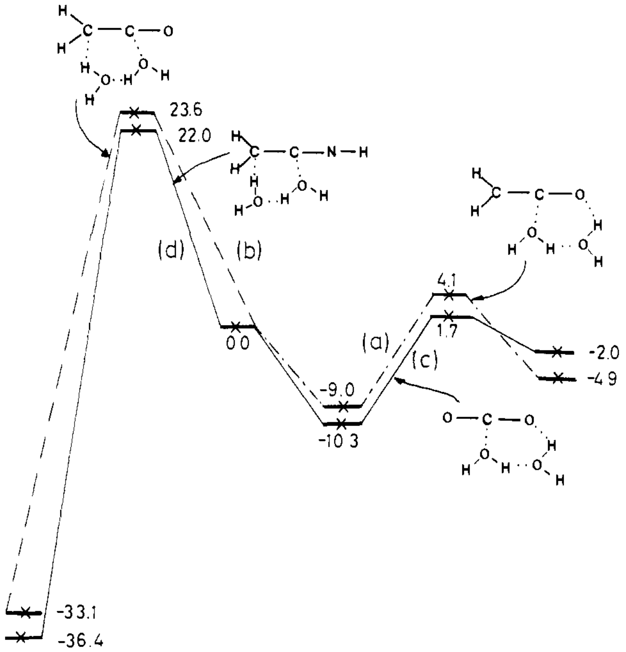


Figure 4. Energy diagrams for the addition of $(H_2O)_2$ to (a) the C=O bond of $CH_2{=}C{=}O$, (b) the C=C bond of $CH_2{=}C{=}O$, (c) the C=O bond of O=C=O, and (d) the C=C bond of $CH_2{=}C{=}NH$. The relative energies are given in kcal mol^{-1} (4-31G basis set) with respect to the cumulene and water dimer systems.

Thus, the addition of the water dimer to the C=O bond of the ketene has an activation energy markedly lower (10 kcal/mol) than that calculated for the addition to the C=C bond. The activation barrier of 13 kcal/mol can be compared with the experimental activation enthalpy of 10.3 kcal/mol as experimentally measured.[7] Moreover, the compact structure of transition state **19** is consistent with the low entropy of activation of −16 eu.[7]

In order to estimate the difference in activation barriers between reaction with the water dimer and water monomer we have also explored the saddle regions of the reaction of $CH_2CO + H_2O$. Although the correct structures of transition states have not been searched, we can estimate approximately the activation energies as 45 and 55 kcal/mol (in STO-3G) for the pathways leading to diol and acetic acid, respectively.

Thus, addition to the C=O bond is again found to be easier than to the C=C bond. However such barriers are much higher than those mentioned above for the addition with the water dimer. Figure 4 illustrates the different pathways of the addition of water dimer to three cumulenes.

From these results we conclude that the water dimer is a realistic model for hydrolysis of these cumulenes in aqueous solutions. On the other hand, it also emphasizes that the preferred hydration pathway with the water dimer of the ketene molecule is via oxygen protonation, in contrast with the thermodynamically more stable carbon protonation.

Table V shows that as the ketene bends, in both transition states, forming or reinforcing the lone pair on the terminal atom (C_β or O), the C_α atom becomes more electrophilic. The charge transfer from the dimer toward the ketene at transition states is noticeably larger in its addition to the C=O bond (0.23 e$^-$) than to C=C bond (0.024 e$^-$). The dipole moments of transition states **18** and **19** are calculated to be 1.14 and 3.94 D (STO-3G), respectively. Transition state **19** appears as the most polar; however, the dipole moment of 3.94 D is slightly larger than the sum of the dipole moments of isolated systems (μ ketene = 0.84 D; μ water dimer = 2.85 D). In effect, one can expect an enhanced addition to the C=O bond in polar solvents.

Although the C_β-protonated and O-protonated transition states present structural similarities, the electronic reorganization along

Table V. Net Charges Along the Pathway of the Reactions between CH_2CO and $(H_2O)_2$

		reaction A		reaction B	
atom	reactants	$18^{\ddagger}$	$CH_3COOH + H_2O$	$19^{\ddagger}$	$CH_2{=}C(OH)_2 + H_2O$
C_α	0.259	0.365	0.316	0.315	0.243
C_β	−0.246	−0.334	−0.207	−0.279	−0.219
O	−0.186	−0.187	−0.271	−0.362	−0.277
H	0.087	0.066	0.083	0.042	0.053
H(H')	0.087	0.066	0.083	0.055	0.071
O_1	−0.415	−0.379	−0.293	−0.357	−0.294
H_1	0.212	0.256	0.183	0.305	0.183
$H(O_1)$	0.159	0.178	0.203	0.227	0.213
O_2	−0.365	−0.414	−0.366	−0.401	−0.366
H_2	0.204	0.226	0.086	0.254	0.210
$H(O_2)$	0.204	0.157	0.183	0.199	0.183

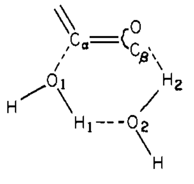
Table VI. Sizes of the Charge Centroids of LMO Participating in the Cyclic Electronic Movements

	$n(O_1)$, $\sigma(C_\alpha O_1)$	$\pi(C_\alpha C_\beta)/\pi(C_\alpha O)$, $\sigma(C_\beta H_2)//n(O)$	$n(O)$, $\sigma(OH_2)$	$\sigma(O_2H_2)$, $n(O_2)$	$n(O_2)$, $\sigma(O_2H_1)$	$\sigma(O_1H_1)$, $n(O_1)$
reactants	1.10	1.61/1.45	1.21	1.33	1.12	1.32
reaction A						
(‡)	1.17	1.80/		1.34	1.14	1.33
product	1.36	1.52/		1.09	1.35	1.22
reaction B						
(‡)	1.22	/1.44	1.26	1.32	1.16	1.32
product	1.37	/1.20	1.36	1.09	1.35	1.20

Table VII. Overlap Populations, Bond Energies, and Degrees of Evolution of Bonds at Stationary Points Along Two Reaction Pathways of $CH_2CO + (H_2O)_2$ System (STO-3G)

	$C_\alpha C_\beta/C_\alpha O$	$C_\alpha O_1$	$C_\beta H_2/OH_2$	O_1H_1	O_2H_1	O_2H_2
		Overlap Populations, P_{AB}				
reactants	0.580/0.482	0.000	0.000/0.000	0.256	0.000	0.263
reaction A						
‡	0.516/	0.032	0.031/	0.255	0.022	0.255
products	0.349/	0.274	0.384	0.000	0.254	0.000
reaction B						
‡	/0.430	0.096	/0.021	0.247	0.046	0.259
products	/0.289	0.281	/0.258	0.000	0.254	0.000
		Bond Energies, kcal/mol				
reactants	135.3/186.8	0.0	0.0/0.0	111.5	0.0	114.5
reaction A						
‡	119.6/	10.3	7.9/	110.0	9.6	111.0
products	76.5/	80.5	98.4/	0.0	110.6	0.0
reaction B						
(‡)	/15.2	28.9	/9.1	107.6	20.0	112.8
products	/85.8	82.9	/112.3	0.0	110.6	0.0
		Degree of Bond Evolution, %				
reaction A (‡)	26.7/	12.8	8.0/	1.3	8.7	3.0
reaction B (‡)	/34.2	34.9	/8.1	3.5	18.1	1.5

the two reaction pathways is at variance. By means of an analysis of the movement of charge centroids of the localized orbitals (LMO), we can compare below the principal types of bond transformations:



reaction A: addition to C=C bond 10 e⁻ implicated	reaction B: addition to C=O bond 12 e⁻ implicated
$n(O_1) \to \sigma(C_\alpha O_1)$	$n(O_1) \to \sigma(C_\alpha O_1)$
$\pi(C_\alpha C_\beta)$	$\pi(C_\alpha O) \to n(O)$
$\searrow \sigma(C_\beta H_2)$	$n(O) \to \sigma(OH_2)$
$\sigma(O_2H_2) \to n(O_2)$	$\sigma(O_2H_2) \to n(O_2)$
$n(O_2) \to \sigma(O_2H_1)$	$n(O_2) \to \sigma(O_2H_1)$
$\sigma(O_1H_1) \to n(O_1)$	$\sigma(O_1H_1) \to n(O_1)$

Since there is no lone pair at the C_β atom, the π system of C=C bond in reaction A must participate directly in the capture of the proton. The size of the LMO's as defined by

$$Si = (\lambda_{pi}^2 + \lambda_{qi}^2 + \lambda_{ri}^2)^{1/2}$$

where $i_{p,q,r}$ are the eigenvalues of the second-moment tensor $\langle\phi_i|\vec{r}^2|\phi_i\rangle$, provided a convenient measure of the spatial extent of the relevant LMO's (see Table VI). At the transition states, only the lone pair of the O_1 atom of the dimer and the π(C=C) pair become more diffuse. There is no appreciable extension in the size of other electron pairs. Naturally, the extension of $n(O_1)$ and C=C pairs is necessary to populate the region of new bonds.

Using the approximate method described in previous work[20,32] to evaluate the degree of bond formation at the transition state we obtain the values collected in Table VII for the bonds that participate in the cyclic electronic reorganization. At the transition state, the degree of formation of intermolecular bonds is appreciable and more advanced in reaction B. If we consider only two

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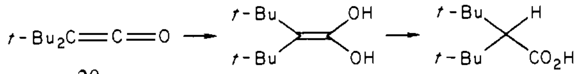
(32) Leroy, G.; Nguyen, M. T.; Sana, M. *Tetrahedron* **1978**, *34*, 2459.

distances $r_1 = C_\alpha O_1$ and $r_2 = C_\beta H_2$ or OH_2, the asynchronization of the reaction as previously defined[20] can be estimated to be 23% and 62%, respectively, for reactions A and B. However the situation is more complicated because of the participation of other evolving bonds. These reactions belong to the concerted (without intermediates) but asynchronous addition type.[20]

Concluding Remarks. Although there is clear evidence from the calculations presented that the preferred mode of addition of water dimer is across the C=O (rather than the C=C) bond of ketene, the implied intermediate (the diol B) has not yet been observed experimentally. Since the technique used to follow the rapid hydration of ketene in one case was ionic conductivity,[7,33] the conversion of the diol, if formed first, to acetic acid (as acetate ion) must be rapid (since the diol would not be detected by using this technique in the pH range studied).



20 21 22

The problem of the reported[34,35] slow reaction of di-*tert*-butylketene (**20**) with water remains. It has been pointed out[34] that proton transfer from H_3O^+ to carbon of the analogous di-*tert*-butyl enol ether is not subject to steric hindrance by the bulky *tert*-butyl groups. A steric effect in proton transfer to oxygen (the preferred transition state as shown by the present work) is even less likely (although the *tert*-butyl group could hinder the approach of the dimer). Hydration across the C=O bond would however give diol **21**, which could be slow to ketonize (to the acid **22**). Thus Hart[36] has pointed out that many enols are relatively stable; the key factor that slows ketonization is steric hindrance, which resists the reduction of the *t*-Bu–C–*t*-Bu bond angle (as in the conversion of **21** to **22**). Thus the slow step with highly sterically hindered ketenes (such as **20**) may be ketonization (**21** → **22**) rather than initial reaction of the ketene (to give diol **21**).

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Registry No. Ketene, 463-51-4.

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An ab Initio CASSCF Study of the Photolytical Formation and Decomposition of Oxathiirane[1]

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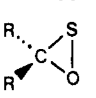
Abstract: Ab initio calculations on the H_2CSO system have been carried out by the CASSCF method. It appears that photolysis of thioformaldehyde *S*-oxide most probably affords rearrangement into the three-membered ring oxathiirane via an excited singlet state. Further photolysis of oxathiirane apparently leads to a weakened S–O bond, the product being best described as a biradiacal, whereas no evidence for a possible ring opening to the corresponding formaldehyde *O*-sulfide was obtained. The wave function of the latter compound seems to be best described as a complex between a distorted sulfur atom and a formaldehyde molecule. On the basis of the calculations the previously reported photolyses of diarylthione *S*-oxides and the corresponding diaryloxathiiranes are discussed.

The appearance of diaryloxathiiranes (**1**, R = Ar) as intermediates in the photolytic conversion of diaryl thioketone *S*-oxides (**4**, R = Ar) has recently been established by low-temperature electronic absorption spectroscopy.[2] Oxathiiranes appeared, not unexpectedly, to be thermally as well as photolytically highly labile compounds, which in both cases produced the corresponding ketones in high yield as reaction products. However, in the photolytic decomposition of diaryloxathiiranes a thermally highly labile intermediate was detected, apparently generated in approximately 10% yield.[2,3] A priori, several compounds could be considered as reasonable candidates, the actual number, however, being reduced to two, the singlet biradial (**2**) and the zwitterionic structure (**3**), partly on the basis of low-temperature ESR spectroscopy and magnetic susceptibility measurements.[3]



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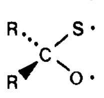

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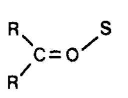

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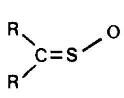

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The intermediate **2**/**3** appeared as a strongly colored compound ($R = C_6H_5$: λ_{max} 550 nm ($\epsilon \approx 11\ 000$)).[2,3] Due to the highly labile nature, it was not possible to obtain, e.g., cycloaddition products with dipolarophiles. The structural assignment of the intermediate was, with this background, left for theoretical considerations. Results from earlier semiempirical MNDO and CNDO/S-CI calculations together with the experimental data

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