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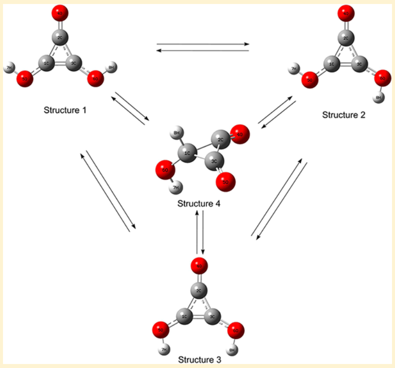
Ab Initio and Density Functional Theory Study of Keto–Enol Equilibria of Deltic Acid in Gas and Aqueous Solution Phase: A Bimolecular Proton Transfer Mechanism

Jovan M. Tadić*,† and Lai Xu‡

†NASA Ames Research Center, Moffett Field, California 94035, United States
‡Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States

S *Supporting Information*

ABSTRACT: Keto–enol tautomerism in deltic acid (2,3-dihydroxycycloprop-2-en-1-one) has been studied using ab initio methods and the B3LYP functional of density functional theory, as well as complete basis set (CBS-QB3 and CBS-APNO) and G4 methods. Relative and absolute energies were calculated with each of the methods, whereas computations of geometries and harmonic frequencies for dihydroxycyclopropenone and hydroxycyclopropanedione were computed in the gas phase but were limited to HF, MP2, and the B3LYP functional, in combination with the 6-31++G(3df,3pd) basis set. Using the MP2/6-31++G(3df,3pd) gas phase optimized structure, each species was then optimized fully in aqueous solution by using the polarizable continuum model (PCM) self-consistent reaction field approach, in which HF, MP2, and B3LYP levels of theory were utilized, with the same 6-31++G(3df,3pd) basis set. In both gas and aqueous solution phases, the keto form is higher in energy for all of the model chemistries considered. From the B3LYP/6-31++G(3df,3pd) Gibbs free energy, the keto–enol tautomeric equilibrium constant for 2,3-dihydroxycycloprop-2-en-1-one/3-hydroxy-1,2-cyclopropanedione is computed to be $K_T(\text{gas}) = 2.768 \times 10^{-12}$ and $K_T(\text{aq}) = 5.469 \times 10^{-14}$. It is concluded that the enol form is overwhelmingly predominant in both environments.



1. INTRODUCTION

Deltic acid was prepared in 1975[1] and belongs to the family of oxocarbons of general formula $C_nH_2O_n$ in which the juxtaposition of a hydroxy group in conjugation with a carbonyl can be thought of as a "vinylogous carboxylic acid"—the proton behaves as if it were attached to a carboxylic acid rather than an alcohol. The acidic proton is on an oxygen connected to an electronegative sp^2-hybridized carbon, increasing its acidity relative to that of a simple alcohol.[2] It has a pK_a of 2.6.[1] As a solid, deltic acid is stable to atmospheric moisture and oxygen, while decomposition can be detected in ethanol–water mixtures after hours but is incomplete even after several days.[3] In the crystal structure determined by X-ray diffraction, the molecules are tied together in strings in the (120) planes in a dimeric fashion and situated across the mirror plane in the crystal. They have C_{2v} symmetry. Each carbonyl group accepts two strong hydrogen bonds.[4] The compound is stable up to 150 °C after gradual heating, but explosive decompositions have also occurred after rapid heating at temperatures as low as 140 °C.[1] The aromaticity of deltic acid and other members of the oxocarbon family is a controversial topic. On the basis of the Hückel π-electron rule and theoretical analysis the aromaticity of deltic acid was proposed even prior to synthesis.[5] However, most recent works first questioned the aromaticity of all oxocarbons above C3[6] and later of both deltic acid and the deltate anion, concluding that they are only weakly aromatic and that large resonance energies and equal bond lengths do not necessarily imply high aromaticity of the molecule.[7] In this work our focus was on a different aspect of this molecule—tautomerism.

Conjugated ketones have been the subject of a number of experimental[8−12] and theoretical studies,[13−20] where their chemical and physical properties have been investigated. One well-known example is the seven-membered species tropolone (2-hydroxy-2,4,6-cyclo-heptatrien-1-one), which has also been studied extensively.[21−30] Tropolone is related to the present study of deltic acid because tropolone may undergo tautomeric equilibriation between the keto and enol forms, as it provides an example of an aliphatic carbonyl compound possessing hydrogens α to the carbonyl group. When such structural features are present, the stabilization resulting from the carbonyl bond generally favors the keto form over the enol. Tropolone, however, is a system that does not follow this pattern and the enol structure is observed almost exclusively. This is attributed to aromaticity present within the enol form, the delocalized ring structure containing six π electrons.[31] Deltic acid, which is a three-membered ring similar to tropolone, is also expected to exist predominantly in the enol form. The purpose of this study is to evaluate the keto–enol

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equilibrium constant for this molecule in both the gas and aqueous solution phases and to confirm the most favored tautomeric structure. To this end, ab initio and density functional theory calculations of the energy and Gibbs free energy have been performed on the dihydroxycyclopropenone−diketone system.

Although a number of measurements of the equilibrium constant for the tautomerization of a variety of keto−enol systems can be found in the literature,[32−36] only relatively few theoretical investigations have been carried out.[37−39] In one study,[38] ab initio HF and MP2 calculations were used to compute the relative energy differences between phenol and 2,4- and 2,5-cyclohexadienone. The equilibrium constant for phenol ⇆ 2,4-cyclohexadienone was evaluated to be 1.98×10^{-13}. This is in excellent agreement with the experimentally determined value of 1.86×10^{-13}, demonstrating that the direction of the equilibrium is strongly in favor of the enol structure. In another investigation[39] using the CBS-QB3 method, a value of 7.15×10^{-14} was computed. From these works it may be safe to conclude that electronic structure methods may be used to compute accurate and reliable relative energies of different tautomeric forms and to evaluate the equilibrium constant for tautomerization.

2. COMPUTATIONAL DETAILS

Ab initio[40] and density functional theory[41] calculations were carried out in the ground singlet state of deltic acid and hydroxycyclopropanedione both in the gas phase and in aqueous solution. The former approach involved HF and MP2 levels of theory (with all electrons treated in the last method), whereas in the latter description the B3LYP[42,43] functional was used entirely. The standard 6-31++G(3df,3pd) basis set[44] was used throughout. A similar study on 2-hydroxy-2-cyclopropen-1-one showed that the selected basis set was large enough and the calculated relative energies were accurate by comparing results to those obtained using two complete basis set approaches, CBS-QB3 and CBS-APNO, as well as the G4 method.[45] For comparison purposes we used CBS-QB3, CBS-APNO, and G4 methods[46] as well. All of the calculations in this study have been performed using the Gaussian 09[47] program.

For each of the species investigated, using the appropriate symmetry as the only constraint imposed, geometries were optimized fully in the gas phase at each model chemistry. This is named as the minimum energy structure, which is located together with a calculation of the vibrational frequencies. The latter calculation is necessary not only to ensure that the optimized geometry corresponds to a local minimum but also to generate thermochemical data to be used in the calculation of equilibrium constants, as well as for a comparison with recorded infrared spectra.

Solvent effects were studied by performing self-consistent reaction field (SCRF) calculations using the polarizable continuum model (PCM)[48] on the MP2(full)/6-31++G-(3df,3pd) gas phase optimized geometry of each species. In this method, the solute is placed into a cavity within the solvent and the latter is modeled as a continuum of uniform dielectric constant. Only one strongly polar solvent, namely water, was studied. Because analytical gradients are available for a number of theoretical levels using PCM, the geometries of each molecule were optimized fully in aqueous solution at the HF, MP2(full), and B3LYP levels.

The changes in total energy, enthalpy (ΔH), and Gibbs free energy (ΔG), at a temperature T of 298.15 K are readily obtained from the results of electronic structure calculations. The Gibbs free energy is given by $\Delta G = \Delta H - T\Delta S$, where ΔS is the change in entropy. The equilibrium constant for tautomerization, K_T, is directly related to the Gibbs free energy, being defined by

$$K_T = \exp(-\Delta G/RT) \tag{1}$$

with $pK_T = -\log K_T$.

3. RESULTS AND DISCUSSION

Ab initio and density functional theory calculations were performed on four structural isomers of $C_3H_2O_3$, whose molecular structures are illustrated in Figure 1, together with their atomic center numbers. They comprise three dihydroxycyclopropenonone structures, corresponding to the enol form, and are labeled **1**−**3** and diketo form **4**. They differ in the orientation of the hydroxy group hydrogen atoms. In structure **1** the MP2(full)/6-31++G(3df,3pd) gas phase optimized $C_3-O_6-H_8$ bond angle is 108.261°, whereas for structures **2** the $C_3-O_6-H_8$ and $C_1-O_5-H_7$ angles are 109.007 and 108.238°, respectively, and for structure **3** the angle is 109.826°. Structures **2** and **4** belong to the C_s point group, while structures **1** and **3** have C_{2v} symmetry.

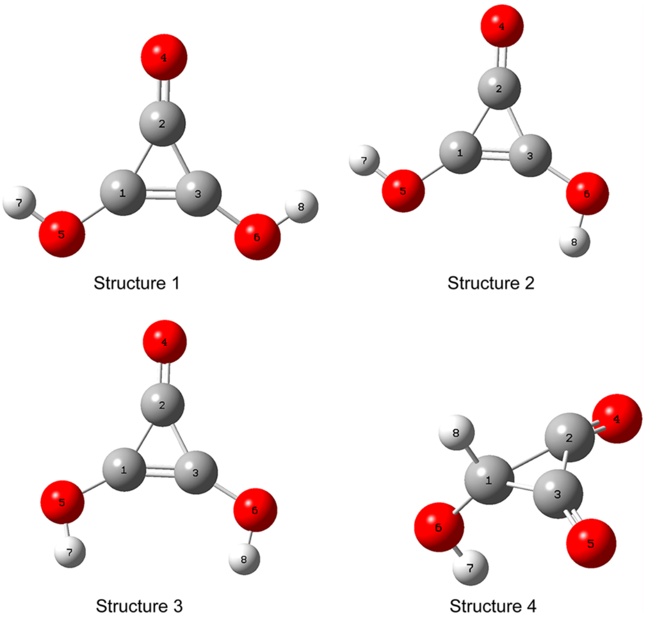

Figure 1. Tautomerization of deltic acid. In enol structure **1** the $C_3-O_6-H_8$ bond angle is 108.261° at MP2/6-31++G(3df,3pd). In the second enol structure (**2**) the $C_3-O_6-H_8$ and $C_1-O_5-H_7$ angles are 109.007 and 108.238°, respectively. In the third enol structure (**3**) the $C_3-O_6-H_8$ bond angle is 109.826°. Structure **4** is the diketone.

Results are given in Tables 1 and 2 for the absolute and relative electronic energies in the gas phase and in aqueous solution, respectively, computed at HF, MP2, and B3LYP-DFT, using the 6-31++G(3df,3pd) basis set. The polarizable continuum model was used to calculate the effect of the solvent. At each model chemistry considered, and for both phases, the keto form is higher in energy than the three enols. For instance, in the gas phase at the MP2 level hydroxycyclopropanedione is 18.89 kcal mol^{-1} higher in energy

Table 1. Gas-Phase Absolute Electronic Energies (au) and Relative Energies (kcal mol^{-1}) for Dihydroxycyclopropenone (Species 1−3) and Hydroxycyclopropanedione (Molecule 4), Evaluated at Different Levels of Theory, with the 6-31++G(3df,3pd) Basis Set[a]

species	HF	MP2	B3LYP	CBS-QB3	CBS-APNO	G3	G4
1	−339.319 15	−340.499 34	−341.149 83	−340.656 74	−341.045 66	−340.913 89	−340.976 09
2	+1.46	+1.40	+1.39	+1.38	+1.29	+1.38	+1.36
3	+4.96	+4.77	+4.64	+4.82	+4.37	+4.84	+4.76
4	+24.60	+18.89	+17.63	+15.63	+15.69	+15.45	+14.83

[a] Also included are corresponding results obtained using the CBS-QB3, CBS-APNO, G3, and G4 methods.

Table 2. Absolute and Relative Electronic Energies in au and kcal mol^{-1}, Respectively, at Different Levels of Theory for the Four Molecules in Aqueous Solution Using the Polarizable Continuum Solvent Reaction Field Model, with the 6-31++G(3df,3pd) Basis Set

species	HF	MP2	B3LYP
1	−339.3379	−340.5114	−341.1657
2	+0.31	+0.42	+0.45
3	+0.75	+1.07	+1.00
4	+28.11	+22.59	+21.02

than species **1**; this difference increases to 22.59 kcal mol^{-1} in the liquid medium. In general, the relative energy between keto and enol increases in solution in comparison to that found in the gas phase.

Table 3 presents the gas and aqueous solution phase Gibbs free energy differences, evaluated at a temperature of 298.15 K and a pressure of 1 atm, at HF, MP2, and B3LYP levels of theory. The trends are similar to those observed for electronic energies. It is noted that the 6-31++G(3df,3pd) basis set is large enough and the differences in relative energy and Gibbs free energy change little by using complete basis set methods. This is consistent with the study by Paine et al.[45] The small differences in Δ*G*, however, will have a large effect on the value of the equilibrium constant (see below).

Table 3. Gas (g) and Aqueous Solution Phase (PCM) Gibbs Free Energy Differences (in au and kcal mol^{-1}) Evaluated at 298.15 K and 1 atm for the Four Molecules at Different Levels of Theory with the 6-31++G(3df,3pd) Basis Set[a]

	1	**2**	**3**	**4**
HF (g)	−339.294 44	+1.39	+4.66	+22.21
MP2 (g)	−340.478 64	+1.32	+4.42	+16.51
B3LYP (g)	−341.130 25	+1.28	+4.28	+15.77
CBS-QB3 (g)	−341.172 09	+1.09	+4.27	+14.36
CBS-APNO (g)	−341.074 666	+1.29	+4.30	+15.26
G3 (g)	−339.225 94	+1.13	+4.63	+17.55
G4 (g)	−341.102 62	+1.08	+4.02	+15.18
HF (PCM)	−339.313 44	+0.29	+0.87	+26.05
MP2 (PCM)	−340.493 67	+0.43	+1.13	+20.25
B3LYP (PCM)	−341.146 03	+0.38	+1.02	+18.09

[a] Also included are the corresponding results obtained with the use of CBS-QB3, CBS-APNO, G3, and G4 methods in the gas phase.

Table 4 displays optimized bond lengths and angles for the four molecules in aqueous solution calculated with PCM at the MP2(full)/6-31++G(3df,3pd) model chemistry. We see very little difference by comparing these results with those obtained in the gas phase at the same level.

Comparable bond lengths are found to agree to within 0.02 Å, whereas respective bond angles differ by no more than 1°. From Table 4, the structural differences between the keto and enol forms are large. Two different types of carbon−oxygen bond lengths occur in the enols, e.g. C_3-O_6 and C_2-O_4 in structure **1**. Due to symmetry, both in enols and in the diketo form, two of the three carbon−carbon bond lengths are identical. The order of the relative energies for the four species may be related to characteristic structural features. In particular, the relative stability in these isomers is influenced largely by the relative positions of the two hydrogen atoms H7 and H8: whether both are bonded to oxygen atoms for enols or one is bonded to carbon and the other to oxygen for structure **4**.

Table 5 has two parts. The first part gives the equilibrium constant when the three enol structures are compared in both gas and aqueous solution phase. The second part gives tautomeric equilibrium constants for the keto form relative to these two isomers, using the Gibbs free energy evaluated at the B3LYP/6-31++G(3df,3pd) level and eq 1. It also gives the corresponding reciprocal constants and values of $pK_i = -\log K_i$ (i = eq (equilibrium), T (tautomerism)). The corresponding gas phase CBS-APNO results for structures **1** and **4** are also presented. It is clear that dihydroxycyclopropenone exists predominantly in the enol form with the ratio of enol (**1**) to the keto form (**4**) being approximately (3.6124×10^{11}):1 in the gas phase at the B3LYP/6-31++G(3df,3pd) model chemistry. With the CBS-APNO method, this ratio changes to (1.5356×10^{11}):1, illustrating the importance of computing highly accurate free energy differences. In the solution phase the equilibrium is driven more strongly in favor of the enol structures. The PCM approach yields $K_T = 5.469 \times 10^{-14}$ for **4** versus **1**, 1.040×10^{-13} for **4** versus **2**, and 3.051×10^{-13} for **4** versus **3**. These are differences of 1.7, 2.4, and 4.1 in pK_T values, respectively, at the B3LYP/6-31++G** level obtained in the gas phase. The extra stability of the enol in aqueous solution is partially attributed to its greater polarity. This is confirmed by comparing the MP2(full)/6-31++G(3df,3pd) computed dipole moments using PCM. For species **1−3**, the dipole moments are 3.32, 6.84, and 9.74 D, whereas for structure **4** it is calculated to be 2.69 D. For comparison, the molecular electric dipole moment for cyclopropenone[8] was measured by Stark shift to be 4.39 D.

In addition to resonance stabilization, the greater polarity of dihydroxycyclopropenone, as reflected in its electric dipole moment, accounts for the predominance of the enol form over the keto structure in aqueous solution, as well as for the difference between the gas and solution phase equilibrium constants.

It is interesting to compare the gas phase results obtained in this study with those previously calculated for phenol.[38] In the present case, from Table 5 the pK_T for structure **1** relative to hydroxycyclopropanedione (**4**) is 11.6 compared to a value of

Table 4. PCM MP2(full)/6-31++G(3df,3pd) Calculated Optimized Geometry (Bond Lengths in Å and Angles in deg) in Aqueous Solution for the Three Isomers of $C_3H_2O_3$

1		2		3		4	
C2–O4	1.2183	C2–O4	1.2289	C2–O4	1.2196	C2–O4	1.1923
C3–C2	1.4275	C3–C2	1.4206	C3–C2	1.4221	C3–C2	1.5527
C3–O6	1.3190	C3–O6	1.3178	C3–O6	1.3176	C3–O5	1.1923
O6–H8	0.9629	O6–H8	0.9639	O6–H8	0.9639	C1–C2	1.5100
C1–C2	1.4275	C1–C2	1.4294	C1–C2	1.4221	C1–O6	1.3628
C1–O5	1.3190	C1–O5	1.3188	C1–O5	1.3176	O6–H7	0.9615
O5–H7	0.9629	O5–H7	0.9630	O5–H7	0.9638	C1–H8	1.0961
C1–C3	1.3520	C1–C3	1.3548	C1–C3	1.3584	C1–C3	1.5200
A(4,2,3)	151.734	A(4,2,3)	151.811	A(4,2,3)	151.475	A(4,2,3)	144.078
A(2,3,6)	153.927	A(2,3,6)	148.017	A(2,3,6)	148.333	A(2,3,5)	144.092
A(3,6,8)	109.056	A(3,6,8)	109.493	A(3,6,8)	109.709	A(4,2,1)	145.435
A (4,2,1)	151.734	A(4,2,1)	151.422	A(4,2,1)	151.467	A(2,1,6)	136.300
A(2,1,5)	153.927	A(2,1,5)	154.487	A(2,1,5)	148.316	A(2,1,8)	99.110
A(1,5,7)	109.056	A(1,5,7)	109.051	A(1,5,7)	109.659	A(1,6,7)	108.780
A(5,1,3)	144.339	A(5,1,3)	144.226	A(5,1,3)	150.211	A(8,1,3)	99.101
A(1,3,6)	144.339	A(1,3,6)	150.037	A(1,3,6)	150.198	A(1,3,5)	145.441
A(1,2,3)	56.532	A(1,2,3)	56.767	A(1,2,3)	57.058	A(1,2,3)	59.288
A(1,3,2)	61.734	A(1,3,2)	61.946	A(1,3,2)	61.470	A(1,3,2)	59.282
A(2,1,3)	61.734	A(2,1,3)	61.287	A(2,1,3)	61.473	A(2,1,3)	61.430

[a] See Figure 1 for atomic center numbers.

Table 5. Gas and Aqueous Solution Phase Equilibrium Constants, Reciprocal Equilibrium Constants, and p*K* Values between the Various Isomeric Forms of $C_3H_2O_3$, Evaluated at the B3LYP/6-31++G(3df,3pd) Level

	K	K^{-1}	pK
	Gas Phase		
4 versus **1**	2.768×10^{-12}	3.612×10^{11}	11.558
4 versus **2**	2.392×10^{-11}	418.069×10^{8}	10.621
4 versus **3**	3.784×10^{-9}	264.250×10^{6}	8.422
3 versus **1**	7.315×10^{-4}	13.670×10^{2}	3.136
3 versus **2**	6.321×10^{-3}	158.210	2.199
2 versus **1**	1.157×10^{-1}	8.641	0.936
	CBS-APNO (g)		
4 versus **1**	6.512×10^{-12}	1.536×10^{11}	11.186
	PCM		
4 versus **1**	5.469×10^{-14}	1.828×10^{13}	13.262
4 versus **2**	1.040×10^{-13}	9.613×10^{12}	12.983
4 versus **3**	3.051×10^{-13}	3.277×10^{12}	12.515
3 versus **1**	0.179	5.579	0.747
3 versus **2**	0.341	2.933	0.467
2 versus **1**	0.526	1.902	0.279

12.7 for the phenol–cyclohexadienone system. In a recent study on hydroxycyclopropenone by Paine et al.,[45] it was argued that the fact that the pK_T value for diketone-enol system was only 5.6 in case of hydroxycyclopropenone points to the "pseudoaromatic" character of that compound, in comparison to the fully aromatic character of phenol. Dihydroxycyclopropenone is derived from the same structure as hydroxycyclopropenone, but the difference here is much smaller. Thus, we doubt that conclusion. The disruption of the coplanar structure of molecule in structure **4**, as well as prevention of full resonance stabilization, may be an explanation itself. Furthermore, in another recent study it was concluded that substituents have very little effect on aromaticities/antiaromaticities of cyclopropene rings with exocyclic double bonds.[7] We showed that significant differences can be found in diketone–enol pK_T values depending on the substituents. This supports the conclusion that the presence of aromaticity itself is not directly correlated to high pK_T values in tautomerism. In the same study,[7] it was also concluded that both deltic acid and its conjugate base, deltate dianion, are only weakly aromatic. New criteria were developed for the characterization of aromaticity, which is beyond the scope of this study. In contrast, in the previous study it was stated that deltate dianion, $C_3O_3{}^{2-}$, is aromatic on the basis of an estimation of the electron delocalization energies and that aromaticity decreases with increasing ring size.[6] Nevertheless, the direction of equilibrium is pushed greatly in favor of the enol structures, due to the additional stabilization afforded by aromaticity and other types of stabilizations in dihydroxycyclopropenone, even overriding the effects of ring strain.

Generally, the reason deltic acid possesses aromatic character is most simply understood on the basis of elementary Hückel molecular orbital theory.[31] Figure 1 shows the conventional depiction of the enols **1–3**. These structures are not aromatic, however. The three-membered ring contains three π electrons. The aromatic forms are illustrated in Figure 2. In this sense, dihydroxycyclopropenone is pseudoaromatic and has a combination of nonaromatic and aromatic resonance structures. The enols therefore have a cyclopropenone structure that satisfies the $4n + 2$ rule, with $n = 0$ in this case corresponding to a delocalized ring system with two π electrons. It is well-known that such cyclic species have extra aromatic stability. The keto

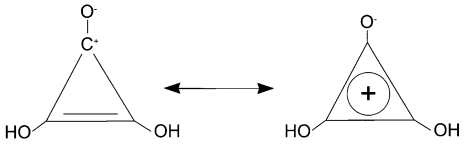

Figure 2. Aromatic resonance forms of dihydroxycyclopropenone.

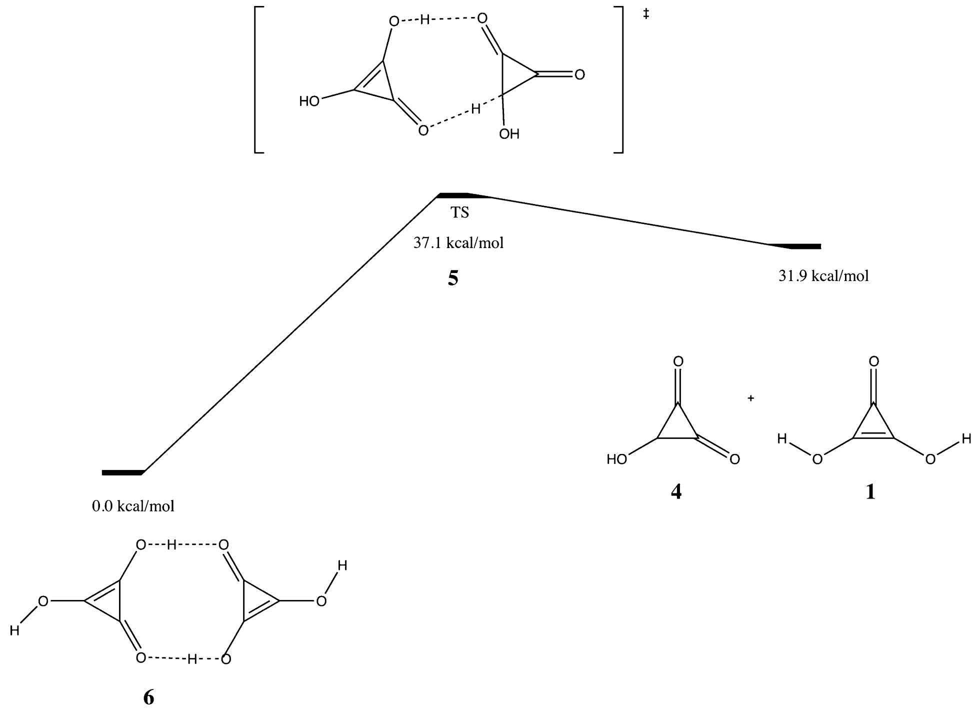

Figure 3. Free energy scheme of the reaction of enol−keto transformation. The reactant is an enol dimer, the transition state is the proton transfer transition state, and the product is mixture of enol and keto forms. The geometries were optimized at the B3LYP/6-31++G(3df,3dp) level.

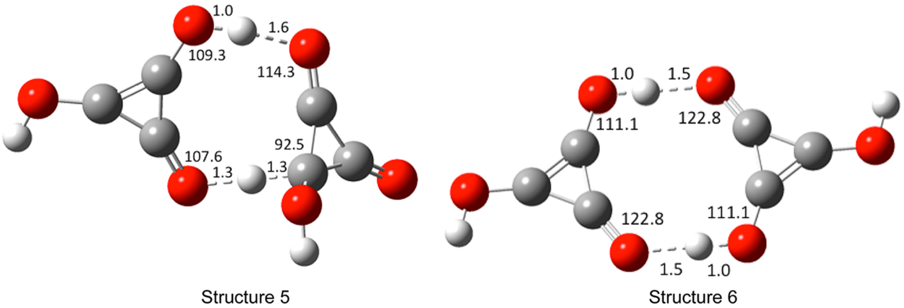

Figure 4. Transition structure **5** connecting structures **1**−**3** and **4**. The geometries of structures **5** and **6** were optimized at the B3LYP/6-31++G(3df,3dp) level.

isomer (**4**) on the other hand, with its methylene group, does not. As in cyclopropenone,[8] the effect of the carbonyl group in the enol is to withdraw electrons from the ring into the polar C═O bond, resulting in the two-π-electron configuration. This is confirmed by considering Mulliken atomic charges in dihydroxycyclopropenone. For O_4 and C_2 atoms in structure **1** at the MP2(full)/6-31++G(3df,3pd) model chemistry in the gas phase, these are computed to be −1.16 and +0.56, respectively, giving rise to a polar carbonyl bond.

In one recent study,[20] newly developed computational criteria for aromaticity were applied to fulvenes, ketocyclopolyenes, fulvenones, diazocyclopolyenes, and their cations. These criteria included magnetic susceptibility exaltations, isomerization energies, aromatic stabilization energies, and nucleus-independent chemical shifts. It was found that the trends observed from these new measurements agreed with those predicted by Hückel theory. Although these new methods could be applied to the systems of interest in this study, they are beyond the scope of the present work but could, nonetheless, form the basis of a future investigation.

Transition State. The reaction mechanism has been explored by locating the stationary point on the potential energy surface at the B3LYP/6-31++G(3df,3dp) level. The reaction involves reactant **6** (enol dimer), transition state **5**, and the product (a mixture of keto **4** and enol **1**). The products cannot be keto dimers, because it is impossible to form a hydrogen bond between C and H. The keto dimer is not stable, leading to the direct formation of enol **1** and keto **4**. The free energy profile of the reactant, transition state, and product is shown in Figure 3. The free energy activation barrier is 37.1 kcal/mol. The free energy of products is lower than that of the transition state by 5.2 kcal/mol.

Figure 4 shows optimized geometries of transition state **5** and reactant **6**. As shown in Figure 4, transition state **5** is a bimolecular hydrogen transfer transition state. The transition state is composed of one enol and one keto form, connected by hydrogen bonds. For one O−H−O hydrogen bond, the two O−H distances are 1.0 and 1.6 Å, respectively. For the other O−H−C hydrogen bond, the O−H distance is 1.3 Å and the C−H distance is 1.3 Å. The reactant **6** is an enol dimer, where two enols are connected by two O−H−O hydrogen bonds. For both hydrogen bonds, the two O−H distances are 1.0 and 1.5 Å, respectively.

In conclusion, the reaction mechanism was investigated by exploring the potential energy surface at the B3LYP/6-31+ +G(3df,3dp) level. The proposed mechanism involves reactant enol dimer **6**, bimolecular hydrogen transfer transition state **5**, and the product (a mixture of keto **4** and enol **1**). The activation free energy activation barrier for the proposed mechanism is 37.1 kcal/mol.

■ ASSOCIATED CONTENT

S Supporting Information

Tables giving Cartesian coordinates of four structures of deltic acid and text giving the full reference for Gaussian 09, Revision A.1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jotadic@lycos.com.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dr. Ivan Juranić.

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